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Environmental Pollution Control Pulp and Paper Industry. Part I. Air

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This publication, directed towards the process and design engineer, describes types, quantities, and sources of emissions, presents the latest control device alternatives, and estimates costs for implementing the air pollution control systems. Emphasis is placed on explanation of chemical and physical processes which generate emission in specific unit operations so that the advantages and disadvantages of both internal and external process control methods can be understood. Actual field installations have provided the basis for the majority of design data.

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NOTICE

The mention of trade names of commercial products in this publication is for illustration purposes and does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency. This manual is presented as a helpful guide to the user and should in no way be construed as a regulatory document.

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FOREWORD

The formation of the United States Environmental Protection Agency marks a new era of environmental awareness in America. The Agency's goals are national in scope and encompass broad responsibility in the area of air and water pollution, solid wastes, pesticides, and radiation. A vital part of EPA's national pollution control effort is the constant development and dissemination of new technology.

It is now clear that only the most effective design and operation of air, water, and solids waste control facilities, using the latest available techniques, will be adequate to meet the future air and water quality objectives and to ensure continued protection of the nation's environment. It is essential that this new technology be incorporated into the contemporary design of pollution control facilities to achieve maximum benefit of our pollution control expenditures.

The purpose of this manual is to provide the pulp and paper industry engineering community with a new source of information for use in the planning, design, and operation of present and future control facilities. It is recognized that there are a number of design manuals, manuals of standard practice, and design guidelines currently available in the field that adequately describe and interpret current engineering practices as related to traditional environmental control design concepts. It is the intent of this manual to supplement this existing body of knowledge by describing new pollution control methods and by discussing the application of new techniques for more effectively removing a broad spectrum of contaminants from air and water discharges. This manual contains two parts; the first describes air pollution control, while the second presents water and solid waste pollution control for the pulp and paper industry.

Much of the information presented is based on the evaluation and operation of pilot, demonstration, and full-scale plants. The design criteria thus generated represent typical values. These values should be used as a guide and should be tempered with sound engineering judgment based on a complete analysis of the specific application.

This manual will be updated as warranted by the advancing state-of-the-art to include new data as they become available and to refine design criteria as additional full-scale operational information is generated. Part I of this manual, Air Pollution Control, is presented herein. Part II, Water and Solids Pollution Control, is currently in preparation and will shortly be available for inclusion into this manual.

CHAPTER 1

INTRODUCTION

From about 1965 to 1975, air pollution technology in the United States pulp and paper industry has undergone major advancements in the design of pollution abatement systems for controlling gaseous and particulate emissions. These technological advances are particularly significant in the kraft pulping segment of the pulp and paper industry because reduced-sulfur gas and particulate emissions have been reduced by changes within the production cycle itself.

A major difficulty confronting the design engineer has been the unavailability of the bulk of this emerging practical process design information in a centralized source, such as this manual. The design approach emphasized in this manual combines process control techniques to minimize the formation of air pollutants with treatment methods for removal of air pollutants from process streams and flue gases.

The information presented in this manual is not limited to North America technology, but also includes technology on internal process control in the Scandinavian pulp and paper industry. Particular stress is placed on explanation of the chemical and physical processes that generate air pollutants in specific unit operations so that the advantages and limitations of both internal and external process control methods can be understood.

Most of the concepts presented in this manual have been demonstrated in actual field installations. Some of these design concepts may be superseded by a rapidly advancing technology; others will endure. Future design approaches must properly consider all aspects of the relationship between the process and air pollution. In particular, the design engineer must be cognizant of the rapidly increasing cost of energy and its direct relationship to certain air pollution control measures. Additionally, deviations from design performance, which become more important as emission limitations become more stringent, will be less tolerable.

Chapter 2 through 13 emphasize the air pollution problems of the kraft or sulfate pulping process. Chapter 14 emphasizes the sulfite process. Chapter 15 and 16 discuss air pollution sources in pulp mills that are not a direct part of the pulping process. Chapter 17 discusses process monitoring of air pollutants.

1.1 Gaseous and Particulate Matter Emissions from Kraft Pulp and Paper Mill Process Sources

The United States pulp and paper industry includes more than 360 mechanical and chemical pulp mills of all types. Further, the industry plans to build approximately 40 new mills during the 1970's.

The industry has made a major contribution to our country's effort to control excessive air pollution from its facilities and has in the past cooperated extensively with government regulatory agencies in dissemination of constantly emerging new control technology (1, 2, 3, 4, 5, 6, 7).

The atmospheric emissions from the kraft process include both gaseous and particulate materials. The major gaseous emissions are malodorous reduced sulfur compounds, such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3), and dimethyl disulfide (CH_3SSCH_3); oxides of sulfur (SO_x); and oxides of nitrogen (NO_x). The particulate matter emissions are primarily sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3) from the recovery furnace, and sodium compounds from the lime kiln and smelt tanks.

Both H_2S and the organic sulfides are extremely odorous and are detectable at a concentration of only a few parts per billion. Thus odor control is one of the principal air pollution problems in a kraft pulp mill. Gas volumes released per unit of production vary considerably between individual process units. Most kraft pulp mill flue gas streams contain appreciable amounts of water vapor.

A summary of the major external control techniques for gaseous and particulate emissions from specific kraft pulp mill sources is presented in Table 1-1. Specific applications are described in appropriate sections of the manual.

1.1.1 Reduced Sulfur

The major gaseous emissions from kraft pulp mill sources are the malodorous reduced sulfur compounds, organic nonsulfur compounds, oxides of sulfur and oxides of nitrogen. The malodorous sulfur gases emitted from kraft pulp mill sources all have extremely low odor threshold levels of between 1 and 10 parts per billion (ppb) by volume (8). The most common reduced sulfur compounds emitted from kraft pulp mill sources are H_2S, CH_3SCH_3, and CH_3SSCH_3; other alkyl sulfur compounds can be emitted in small quantities from certain wood species.

The major potential sources for the reduced sulfur gas emissions to the atmosphere include digester blow and relief gases, vacuum washer hood and seal tank vents, multiple-effect

TABLE 1-1
EXTERNAL CONTROL TECHNIQUES FOR GASEOUS AND PARTICULATE MATTER EMISSIONS FROM KRAFT PULP MILL SOURCES

Emission Source	Gaseous Control	Particulate Control
Digester gases	Incineration Condensation	NA (not applicable)
Washer vents	Incineration	NA
Evaporator gases	Incineration Scrubbing Condensation	NA
Condensate water	Steam stripping Air stripping	NA
Condensate Stripper Vent	Incineration	NA
Black Liquor Oxidation Tower Vent	Incineration	NA
Tall Oil Vent	Scrubbing	NA
Recovery Furnance	Scrubbing	Precipitators Scrubbing Filtration
Smelt Tank	Scrubbing	Scrubbing
Lime Kiln	Scrubbing	Scrubbing Precipitators
Slaker Vent	NA	Scrubbing
Bleach Plant	Scrubbing	NA
Paper Machines	Incineration Adsorption Condensation	NA
Power Boilers	NA	Cyclones Precipitators Scrubbing

evaporation hotwell vents, recovery furnace flue gases following direct contact vents, smelt dissolving tanks, slaker vents, black liquor oxidation tank vents, lime kiln exit vents and wastewater treatment operations. Summaries of values on variations in gas flow rates, malodorous sulfur gas concentrations, and emission rates per unit production for the kraft process units are presented in Tables 1-2 to 1-4. These values are based on a variety of sources.

TABLE 1-2
TYPICAL GAS CHARACTERISTICS FOR KRAFT PULP MILL PROCESSES

Emission Source	Process Offgas Characteristic		
	Flow Rate* m^3/t (ft^3/ton)	Temperature °C (°F)	Moisture Content %
Digester, Batch:			
Blow Gases	3-6,000 (96-190,000)	65-100 (150-210)	30-99
Relief Gases	0.3-100 (10-3,200)	25-60 (80-140)	3-20
Digester, Continuous	0.6-6 (20-200)	75-150 (170-300)	35-70
Washer Hood Vent	1,500-6,000 (48,000-190,000)	20-45 (70-110)	2-10
Washer Seal Tank	300-1,000 (9,600-32,000)	55-75 (130-170)	15-35
Evaporator Hotwell	0.3-12 (10-400)	80-145 (180-290)	50-90
BLO Tower Exhaust	500-1,500 (16.000-48,000)	70-80 (160-180)	30-40
Recovery Furnace	6,000-12,000 (190,000-380,000)	120-180 (250-360)	25-35
Smelt Dissolving Tank	500-1,000 (16,000-32,000)	70-110 (160-230)	35-45
Lime Kiln Exhaust	1,000-1,600 (32,000-51,000)	65-95 (150-200)	25-35
Lime Slaker Vent	12-30 (400-1,000)	65-75 (150-170)	20-25

*At standard conditions of dry gas (21.1°C & 760mmHg (70°F & 29.92 in Hg))
Flow in cubic meters per metric ton and (cubic feet per short ton)

TABLE 1-3
TYPICAL REDUCED SULFUR GAS CONCENTRATIONS FROM KRAFT PULP MILL SOURCES

Emission Source	Concentration (ppm by volume) H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3
Digester, Batch:				
Blow Gases	0-1,000	0-10,000	100-45,000	10-10,000
Relief Gases	0-2,000	10-5,000	100-60,000	100-60,000
Digester, Continuous	10-300	500-10,000	1,500-7,500	500-3.000
Washer Hood Vent	0-5	0-5	0-15	0-3
Washer Seal Tank	0-2	10-50	10-700	1-150
Evaporator Hotwell	600-9,000	300-3,000	500-5,000	500-6,000
BLO Tower Exhaust	0-10	0-25	10-500	2-95
Recovery Furnace (after direct contact evaporator)	0-1,500	0-200	0-100	2-95
Smelt Dissolving Tank	0-75	0-2	0-4	0-3
Lime Kiln Exhaust	0-250	0-100	0-50	0-20
Lime Slaker Vent	0-20	0-1	0-1	0-1

Both oxides of sulfur (SO_X) and oxides of nitrogen (NO_X) can be emitted in varying quantities from specific sources in the kraft chemical recovery system. The major source of sulfur dioxide (SO_2) emissions is the kraft chemical recovery furnace, because of combustion of sulfur-containing black liquor fuel. Under certain conditions, somewhat similar quantities of sulfur trioxide (SO_3) can be released to the atmosphere, particularly when residual fuel oil is added as an auxiliary fuel (9). Lesser quantities of SO_2 can also be released from the lime kiln and smelt dissolving tank. Trace quantities of sulfur oxides may also be released from other kraft mill sources. Oxides of nitrogen can be formed in any fuel combustion process by the reaction between oxygen and nitrogen at elevated temperatures.

TABLE 1-4
TYPICAL REDUCED SULFUR GAS EMISSION RATES FROM KRAFT PULP MILL SOURCES

	Emission Rate, kg sulfur per metric ton of air dried pulp			
Emission Source	H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3
Digester, Batch:				
Blow Gases	0-0.1	0-1.0	0-2.5	0-1.0
Relief Gases	0-0.05	0-0.3	0.05-0.8	0.05-1.0
Digester, Continuous	0-0.1	0.5-1.0	0.05-0.5	0.05-0.4
Washer Hood Vent	0-0.1	0.05-1.0	0.05-0.5	0.05-0.4
Washer Seal Tank	0-0.01	0-0.01	0-0.05	0-0.03
Evaporator Hotwell	0.05-1.5	0.05-0.8	0.05-1.0	0.05-1.0
BLO Tower Exhaust	0-0.01	0-0.1	0-0.4	0-0.3
Recovery Furnace (after direct contact evaporator)	0-25	0-2	0-1	0-0.3
Smelt Dissolving Tank	0-1	0-0.8	0-0.5	0-0.3
Lime Kiln Exhaust	0-0.5	0-0.2	0-0.1	0-0.05
Lime Slaker Vent	0-0.01	0-0.01	0-0.01	0-0.01

The major constituent formed in nitric oxide (NO), a small portion of which can be oxidized to form nitrogen dioxide (NO_2): together they are classified as total oxides of nitrogen. Nitrogen oxide emissions from kraft pulp mill process sources, such as the recovery furnace and lime kiln, are normally lower than for most other fuel combustion processes. This is primarily due to the large quantities of water present in black liquor and lime and which act as a heat sink to suppress the flame temperature. Larger quantities of oxides of nitrogen can be formed, however, when auxiliary fuels such as natural gas or fuel oil are added to the recovery furnace.

TABLE 1-5
TYPICAL EMISSION CONCENTRATIONS AND RATES FOR SO_x AND NO_x FROM KRAFT PULP MILL COMBUSTION SOURCES

	Concentration (ppm by vol.)			Emission Rate, kg/t*		
Emission Source	SO_2	SO_3	NO_x (as NO_2)	SO_2	SO_3	NO_x (as NO_2)
Recovery Furnace:						
No Auxiliary Fuel	0-1,200	0-100	10-70	0-40	0-4	0.7-5
Auxiliary Fuel Added	0-1,500	0-150	50-400	0-50	0-6	1.2-10
Lime Kiln Exhaust	0-200	----	100-260	0-1.4	----	10-25
Smelt Dissolving Tank	0-100	----	----	0-0.2	----	----

*kilograms per metric ton of air dried pulp.

A summary of concentrations and emission rates for oxides of sulfur and oxides of nitrogen for specific kraft pulp mill sources is presented in Table 1-5. The information included is based upon a variety of industry sources. The extreme variations in operating conditions that occur in the industry, including operating combustion temperature and type of fuel, account for the broad ranges in these data.

1.1.3 Organic Compounds

Organic compounds other than those containing sulfur can also be emitted in varying quantities from several different kraft pulp mill process sources. The major types of materials that can be released to the atmosphere include terpenes, hydrocarbons, alcohols, phenols and other organic compounds liberated from wood. Additional organic compounds can be produced when organic materials are applied as coatings to paper sheet or can be induced when spent caustic solutions are used as chemical make-up for the process.

The primary significance of these materials is that they may either act directly as odorant gases or as liquid particulate carriers for odorous sulfur gas molecules, particularly the terpene compounds. The olefinic hydrocarbons or terpenes may undergo photochemical reactions in polluted atmospheres.

The major potential process sources of organic nonsulfur compound emissions to the atmosphere include digester blow and relief gases, multiple-effect evaporator noncondensable gases, brown stock washer hood and seal tank vents, black liquor oxidation tower vents, black liquor storage tank vents, direct-contact evaporator exhaust gases, digester and evaporator condensate water vents and wastewater treatment facilities, and paper machine coating and drier vents.

Major process variables that affect emissions of these compounds to the atmosphere include the wood species being pulped or the type of coating material applied, the respective organic or condensate stream temperature, the volatility of the respective organic compounds, and the type and effectiveness of any air pollution control device.

1.1.4 Particulate Matter Emissions

The major potential process sources of particulate emissions from the kraft chemical recovery system are the recovery furnace, the smelt dissolving tank, and the lime kiln. The recovery furnace is the largest potential particulate emission source. The major chemical constituent in the recovery boiler particulate emissions is Na_2SO_4, with smaller quantities of Na_2CO_3 and sodium chloride (NaCl) also present. The smelt dissolving tank vents and lime kiln exhaust gases are also sources of varying quantities of particulate matter consisting primarily of carbonate, hydroxide, sulfate and chloride salts of calcium and sodium. Particle sizes from these sources can range from 0.1 μm (4×10^{-6} in) to greater than 1000 μ (4×10^{-2} in) in diameter for uncontrolled emissions and from 0.1 to 10 μm (4×10^{-6} to 4×10^{-4} in) in diameter where these sources have high efficiency particulate control devices.

The two major types of particulate matter control devices employed for kraft recovery furnaces are electrostatic precipitators (ESP) following cyclone or cascade-type direct contact evaporators, and venturi-type evaporator-scrubbers in a one-or two-stage configuration. Low pressure drop secondary wet scrubbers have been employed to supplement older and less efficient primary particulate collection devices at several existing mills to alleviate particle fallout in areas adjacent to the plant premises. Packed tower or showered mesh demister scrubbers are employed for particulate control on smelt dissolving tank exhaust gases, while venturi or cyclonic scrubbers are normally used for particulate control on lime kiln or fluorosolid calciner exhaust gases. The amount of particulate matter emitted from kraft pulp mill process sources depends both on the process operating conditions and on the types and collection efficiencies of any control devices employed.

A summary of typical ranges in particulate concentrations and emissions rates from kraft pulp mill process sources is presented in Table 1-6.

TABLE 1-6
TYPICAL CONCENTRATIONS AND EMISSION RATES FOR PARTICULATE MATTER FROM KRAFT PULP MILL SOURCES (AFTER CONTROL DEVICES)

Emission Source	Concentration		Emission Rate	
	g/scm	(gr/scf)	kg/t	(lb/ton)
Recovery Furnace:				
After Electrostatic Precipitator	0.06-1.1	(0.03-0.5)	0.5-12	(1.0-24)
After Venturi Evaporator	0.9-2.3	(0.4-1.0)	7-25	(14-50)
Lime Kiln	0.07-1.1	(0.03-0.5)	0.15-2.5	(0.3-5.0)
Smelt Dissolving Tank	0.04-2.3	(0.02-1.0)	0.01-0.5	(0.02-1.0)

1.2 Gaseous and Particulate Emissions from Sulfite Pulp and Paper Mill Process Sources

The primary emissions from the sulfite pulping process are SO_2 and particulate matter. In special cases of burning alkaline sulfite liquor in recovery furnaces under reducing conditions, H_2S emissions may also occur. Otherwise, there are practically no organic reduced sulfur compounds produced in the sulfite process. Nitrogen oxides are emitted from various combustion sources, particularly from the recovery furnace of ammonium-based mills.

1.2.1 Sulfur Dioxide

Various process sources within the sulfite mill can emit SO_2. The main sources are the digester blow pits, multiple-effect evaporators, and liquid burning or chemical recovery systems. Minor process sources include pulp washers and the acid preparation plant. Typical values of SO_2 emission rates are listed in Table 1-7.

1.2.2 Particulate Matter

The recovery furnace is the significant process source of particulate matter in a sulfite pulp mill. Potential particulate matter emissions depend greatly on the degree of recovery of sulfite waste liquor, as well as on the degree of control of particulate matter.

TABLE 1-7
TYPICAL SO_2 EMISSION RATES FROM SULFITE PULP MILL SOURCES

Emission Source	Emission Rate, kg/t (lb/ton)*	
	Uncontrolled	Controlled**
Blow Pit:		
Hot blow	30-75 (60-150)	1-2.5 (1-5)
Cold blow	2-10 (4-20)	0.05-0.3 (0.1-0.6)
Evaporators	1-30 (2-60)	0.025-1 (0.05-2)
Recovery Process	80-250 (160-500)	6-20 (12-40)
Washers	0.5-1 (1-2)	---
Acid Preparation	0.5-1 (1-2)	---

*Per mass, t (ton), of air dried pulp.
**Alkaline scrubbing of gases.

1.2.3 Nitrogen Oxides (NO_x)

In ammonium-based sulfite pulp mills, combustion of the spent sulfite liquor will result in emissions of nitrogen oxides from the recovery furnace. Emissions from one such system ranged from 4.7 kg/t to 11.8 kg/t (9.4 to 23.6 lb/ton).

1.3 Power Boilers

The pulp and paper industry is a major energy consumer in the United States, accounting for about 2.2 percent of the total national energy consumption. This amounts to approximately 1.6×10^{18} J per year (1.5×10^{15} BTU/yr) of which approximately one-half is associated with the manufacture of kraft pulp and paper (10). Typical energy consumption requirements for a kraft pulp mill are about 28.7 GJ per metric ton of air dried pulp (30 million BTU/ton) of which 50 to 60 percent can normally be supplied by combustion of the black liquor solids (11).

For mills employing on site debarking, an additional 20-30 percent of the energy requirement can be supplied by the burning of waste wood in bark boilers. As a result, it is normally necessary for kraft pulp mills to obtain about 5 to 30 percent of their energy requirements by burning supplementary fuels such as coal, fuel oil, and natural gas. The total energy that must be supplied by supplementary combustion of coal, oil, gas, or wood in kraft pulp and paper mill power boilers can range from less than 0.9 million to more than 5.4 GJ per metric ton of pulp (0.75 to 4.5 million BTU per ton of pulp).

The exact energy requirements for the auxiliary fuel burning of coal, oil, gas, or wood will vary between individual mills depending on their respective energy balances, physical characteristics, and availability of fuels in each local area. The major air pollutants of possible concern from auxiliary fuel burning operations include particulate matter from coal and wood, sulfur oxides from coal and fuel oil, and nitrogen oxides from coal, oil, gas, and wood. Available particulate matter control devices for coal and wood-fired power boilers include electrostatic precipitators, liquid scrubbers, fabric filters, and mechanical cyclones. A summary of uncontrolled air pollutant emissions from auxiliary fuel combustion in power boilers in the pulp and paper industry is presented in Table 1-8 (12).

TABLE 1-8
UNCONTROLLED AIR POLLUTANT EMISSIONS FROM FUEL COMBUSTION IN AUXILIARY POWER BOILERS

	Air Pollutant Emission Rate; kg/10^6 kJ (lb/10^6 BTU)			
Air Pollutant	Bituminous Coal*	Residual Fuel Oil**	Natural Gas+	Waste Wood++
Particulate Matter	0.38 (0.95)	0.024 (0.060)	0.005 (0.01)	1.50 (3.75)
Sulfur Oxides (as SO_2)	0.84 (2.1)	0.46 (1.1)	----	0.16 (0.40)
Nitrogen Oxides (as NO_2)	0.39 (0.98)	0.23 (0.58)	0.16 (0.40)	0.43 (1.1)
Hydrocarbons (as CH_4)	0.007 (0.02)	----	0.17 (0.43)	0.11 (0.28)
Carbon Monoxide	0.021 (0.053)	----	----	0.11 (0.28)

*Based on average heating value of 25.7 MJ/kg coal (11,000 BTU/lb)
**Based on average heating value of 41.9 GJ/m^3 oil (150,000 BTU/gal)
+Based on average heating value of 39.1 MJ/m^3 natural gas (1,050 BTU/ft^3)
++Based on waste wood heating values as follows:

Item	Units	Dry Basis	Wet Basis
Moisture Content	% by mass	0.0	50.0
Heating Value	MJ/kg	18.6	9.3
Heating Value	BTU/lb	8000	4000

1.4 References

1.4.1 Cited References

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1.4.2 Additional Reading

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3. Whitney, R. P. (ed.), *Chemical Recovery in Alkaline Pulping Processes,* Tappi Monograph Series No. 32. Technical Association of the Pulp and Paper Industry, New York, New York, 1968.

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CHAPTER 2

DIGESTER GASES

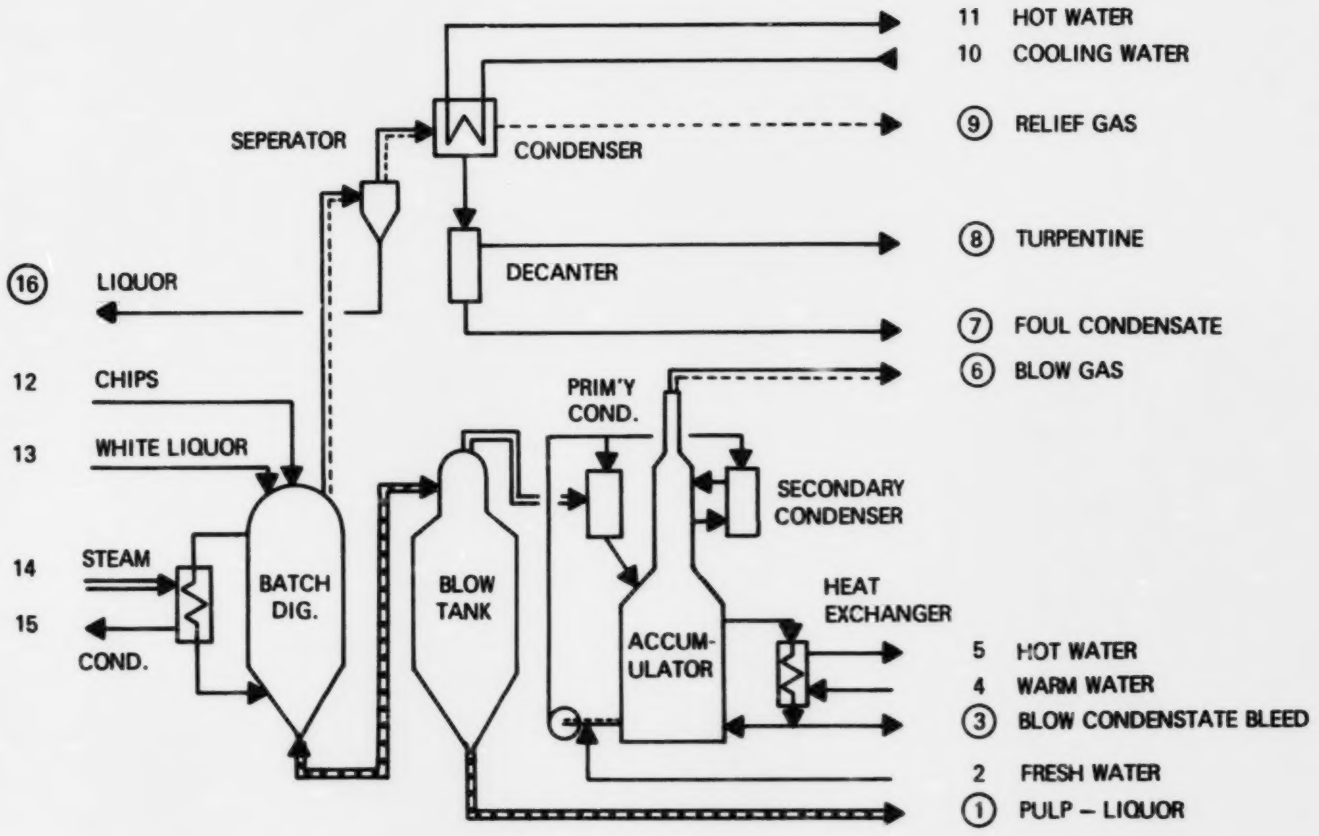
The digestion process is the third most important source of odor pollution in the kraft process. Black liquor combustion and weak black liquor evaporation are first and second, respectively. Gases from the digester contain organic sulfur compounds from reactions between components of the wood and the sulfide of the white liquor. These gases also contain some H_2S, turpentine, and traces of methanol (CH_3OH), ethanol (CH_3CH_2OH), and acetone (CH_3COCH_3), as well as displaced air.

The composition and quantity of digester gases will differ between batch digesters and continuous digesters. Variations will also occur with the type of wood, the sulfide concentration in the white liquor, the final cooking temperature, and the cooking time. Most of these factors are determined by production requirements and vary widely with the production schedule.

The basic method for minimizing odor pollution in the digester area is to effect adequate condensation and to contain the relief and blow gases. As a further step, contained gases may be incinerated. In the following sections important factors in using these methods are discussed.

2.1 Batch Digesters

Batch digesters often present air pollution problems because of surges of gas flow produced during blowing. These surges can temporarily overload the condensing or heat recovery system. Economics of production demand that a plant be operated at full capacity. Often, the capacity of the batch digesters is limited by their condensing systems, so that full-scale production can overload these systems. This problem can be compounded since liquid carryover from short term overloads can increase fouling of the condensing systems; thus, further lowering the capacity and making the systems inadequate for even less than design flows. The condensing system for batch digesters must be designed for peak flows and all components in the heat recovery system must be kept in good operating condition. To allow proper operation, the system must have enough temperature and pressure difference measurements to enable the operator to judge the condition of the system. Figure 2-1 shows a typical batch digester and its blow heat recovery system. Point sources of odor release are indicated in this figure.


11 HOT WATER
10 COOLING WATER
⑨ RELIEF GAS
⑧ TURPENTINE
⑦ FOUL CONDENSATE
⑥ BLOW GAS
5 HOT WATER
4 WARM WATER
③ BLOW CONDENSATE BLEED
2 FRESH WATER
① PULP – LIQUOR
⑯ LIQUOR
12 CHIPS
13 WHITE LIQUOR
14 STEAM
15 COND.
SEPERATOR
CONDENSER
DECANTER
PRIM'Y COND.
SECONDARY CONDENSER
HEAT EXCHANGER
BATCH DIG.
BLOW TANK
ACCUM-ULATOR

POINTS OF POSSIBLE ORDER RELEASE ARE ENCIRCLED BY ○

FIGURE 2-1

BATCH DIGESTER FLOW SHEET

2.1.1 Blow Gases

Batch digester blow gases are a major cause of air pollution. As a rough guide to the volumes that can be expected, a single blow will produce approximately one ton of steam per ton of air dry pulp (90 percent absolute dry fiber). Blowing a 200 m^3 (7100 ft^3) digester to atmospheric pressure from 0.64 MPa (78 psig) produces about 20 t (22 tons) of pulp and 34,000 m^3 (1,200,000 ft^3) of steam within a 20 minute period (Figure 2-2). Effective condensation of this volume of steam requires a blow heat recovery system with adequate capacity and a control system which reacts quickly but retains stability.

The vent from the blow heat accumulator (flow 6 in Figure 2-1) might typically show flow histories as illustrated in Figure 2-3. These flow histories were recorded with a pitot tube. Normally, about 90 percent of the volume is steam, and the noncondensable portion is about 3 m^3 per metric ton of pulp (96 ft^3/ton). Typical flow and composition ranges were given in Tables 1-2 and 1-3. A successful blow gas treatment program starts with an efficient blow heat recovery system (section 2.2.1.1) followed by a flow equalization system and a gas incineration system.

Blow gas flows, such as those shown in Figure 2-3, cases 2 and 3, will overload any reasonable flow equalization system and thus seriously degrade the entire blow gas treatment program. Loss of recoverable heat is also probable in these two cases.

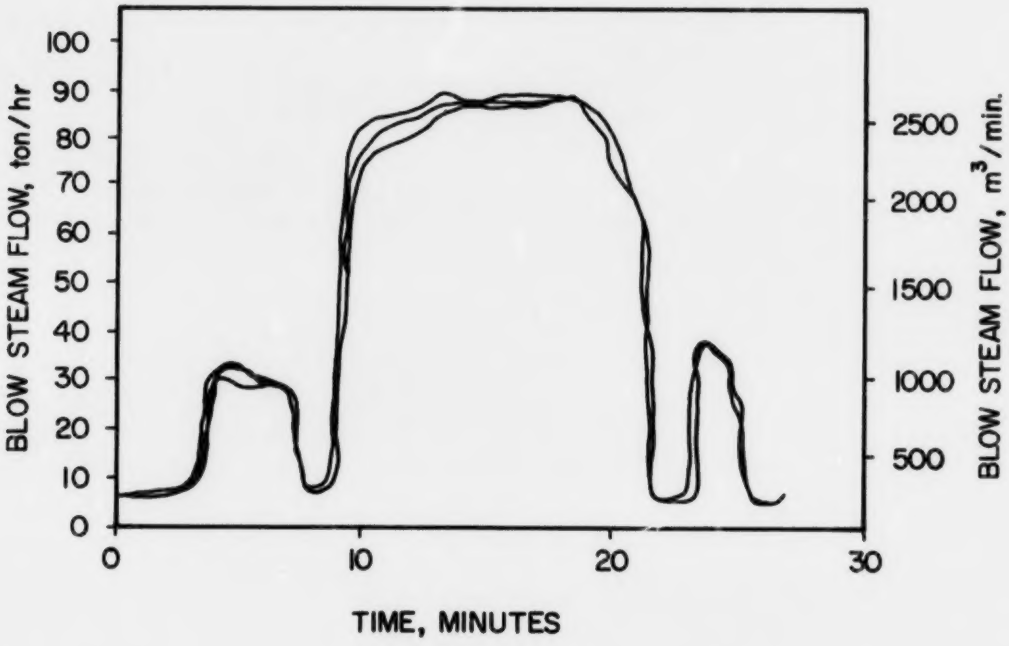
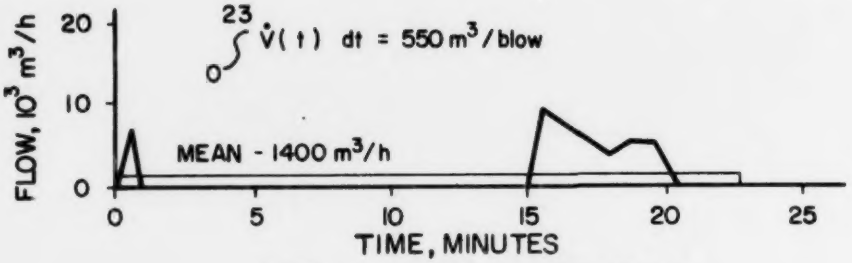
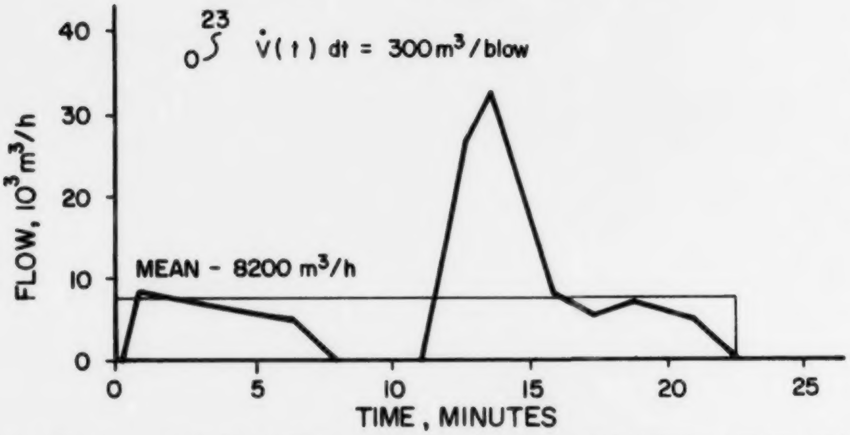


FIGURE 2-2

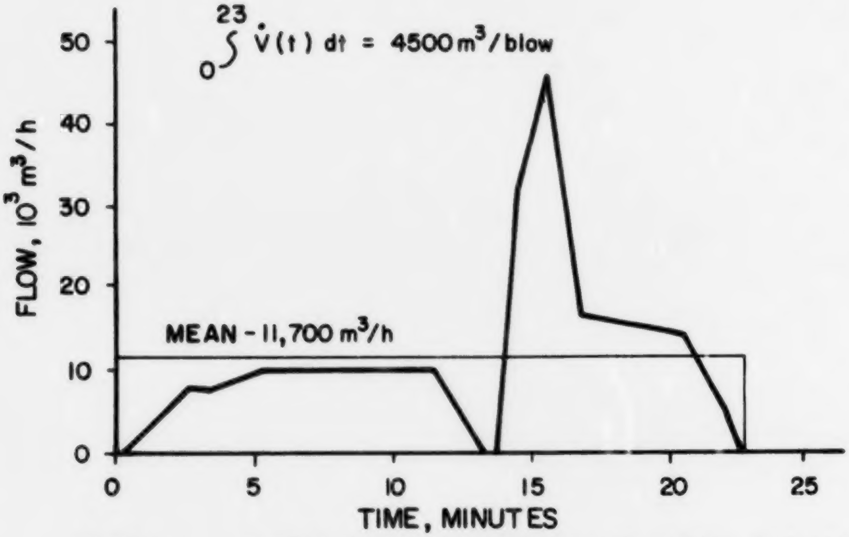
KRAFT BATCH DIGESTER BLOW STEAM FLOW (1)



CASE I. NORMAL OPERATIONS



CASE 2. MALFUNCTION OF BLOW HEAT RECOVERY HEAT EXCHANGERS



CASE 3. INCREASING MALFUNCTION OF HEAT EXCHANGERS

FIGURE 2-3

KRAFT BATCH DIGESTER BLOW GAS FLOW AFTER CONDENSING AND WITHOUT EQUALIZATION (2)

Final odor gas treatment by white liquor scrubbing is not very efficient because of the dominance of nonionizable organic sulfur compounds. Only H_2S and CH_3SH can be efficiently recovered by alkaline scrubbing (Figures 2-4 and 2-5).

Therefore, incineration of the blow gases (section 4.3) after proper gas flow equalization (section 4.2.2) is recommended.

2.1.1.1 Blow Heat Recovery

The blow heat recovery system, as shown in Figure 2-1, and its proper operation will significantly affect the further treatment of both blow gases and blow condensates. Factors that may affect the batch digester air pollution abatement program are final blow pressure, blow tank drop separation, primary blow steam condenser, secondary blow steam condenser, blow heat accumulator and blow heat recovery heat exchanger.

The blow gas flow is directly proportional to the final blow pressure (i.e., the higher the final blow pressure, the more violent the blow gas flow, and the more difficult it is to condense and collect the blow gases for treatment). Decreasing the final pressure, however,

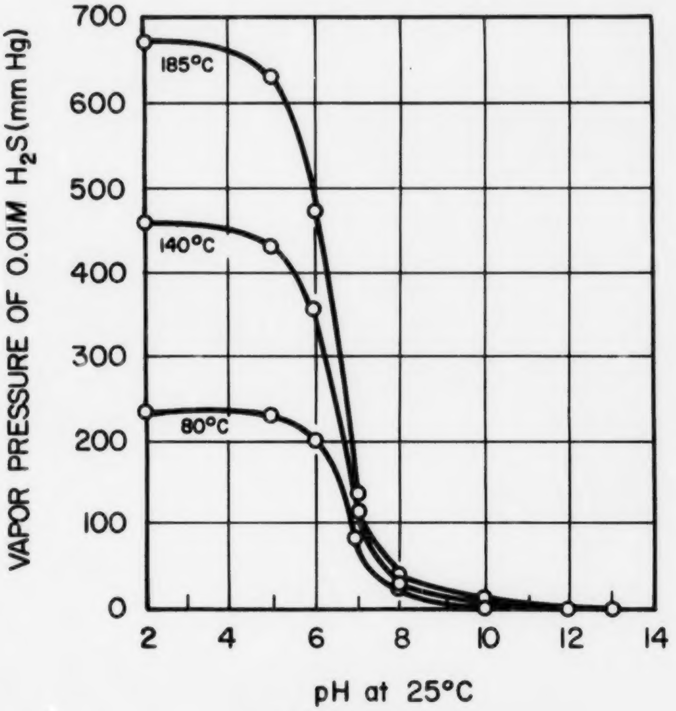


FIGURE 2-4

VAPOR PRESSURE OF 0.01 *M* H_2S VS. pH AT VARIOUS TEMPERATURES (4)

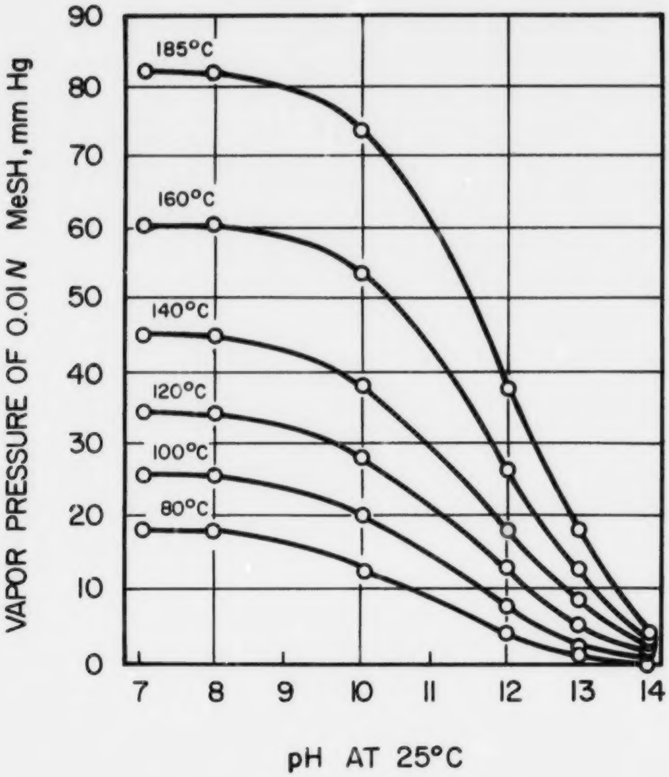


FIGURE 2-5

VAPOR PRESSURE OF 0.01*N* CH_3SH VS. pH
AT VARIOUS TEMPERATURES (4)

may require relief or other operations that take time and consequently decrease production rates. A violent blow also means more fiber and liquor carryover to the heat recovery system with possible fouling of heat exchanger surfaces. Lower blow pressure also gives better pulp quality. Final blow pressure is usually 0.4-0.5 MPa (58-72 psig).

An efficient blow tank drop separator stops fiber and liquor carryover (3). Fiber and liquid carryover fouls filters and heat exchanger surfaces, thereby decreasing heat transfer and increasing pressure drops in the system. A reduction in system capacity results in inferior condensation of blow steam and leads to difficulties in noncondensable blow gas treatment.

The capacity of the blow steam condenser must be sufficient for handling the largest digester, the highest blow pressure, the shortest blow period, the highest water temperature, or any combination of these. This applies as well to the main condenser pump as to the direct contact condenser itself. Usually the addition of cold water to the primary condenser (flow 2 in Figure 2-1) will improve condensation, but will increase the blow condensate bleed (flow 3 in Figure 2-1). A most important factor is the condenser control system.

Usually it is a simple temperature control of the water flow (See Figure 2-6). This control system is too slow for the abrupt beginning of the blow and, when made more sensitive to compensate for speed, it often becomes unstable. No really good solution to this control problem exists. One solution to minimize blow gas treatment problems is to install a feed forward control. This control can be a simple on-command to open the condenser water valve at a specified time before the digester blow valve is opened. This results in lowering the temperature of the hot water produced in the blow heat recovery system (1). Condenser outlet temperature should be kept around 90° C (194° F).

A secondary condenser is very common as a backup for the primary condenser. If properly controlled it will accommodate temporary overloads on the primary condenser, thus facilitating treatment of noncondensable blow gases. It may be either a direct contact condenser or a surface condenser (the latter gives a more concentrated condensate). A suitable condenser outlet temperature (see Figure 2-7) should be around 50° C (122° F).

For the blow heat accumulator, the two determining factors are sufficient size to accommodate large blows and long pauses between blows, and an internal construction that will cause the zone between hot- and cooled-water to be as sharp and undisturbed as possible. Frequently, hot water does find its way down to the bottom of the accumulator, enters the condenser, and thereby drastically reduces the condensing capacity. Subsequent gas handling problems occur.

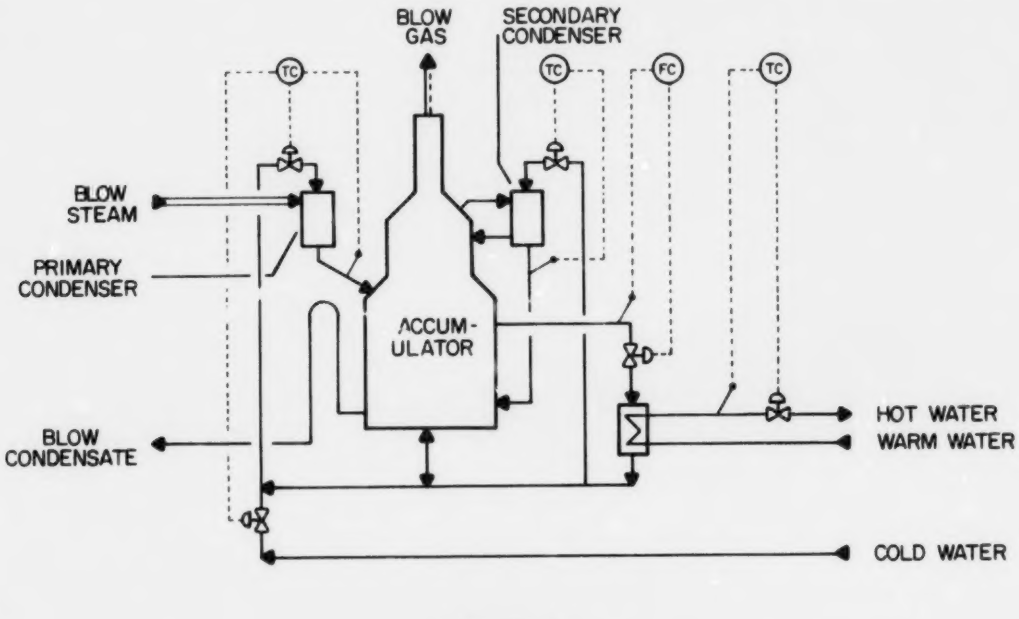


FIGURE 2-6

BLOW HEAT RECOVERY CONTROL SYSTEM

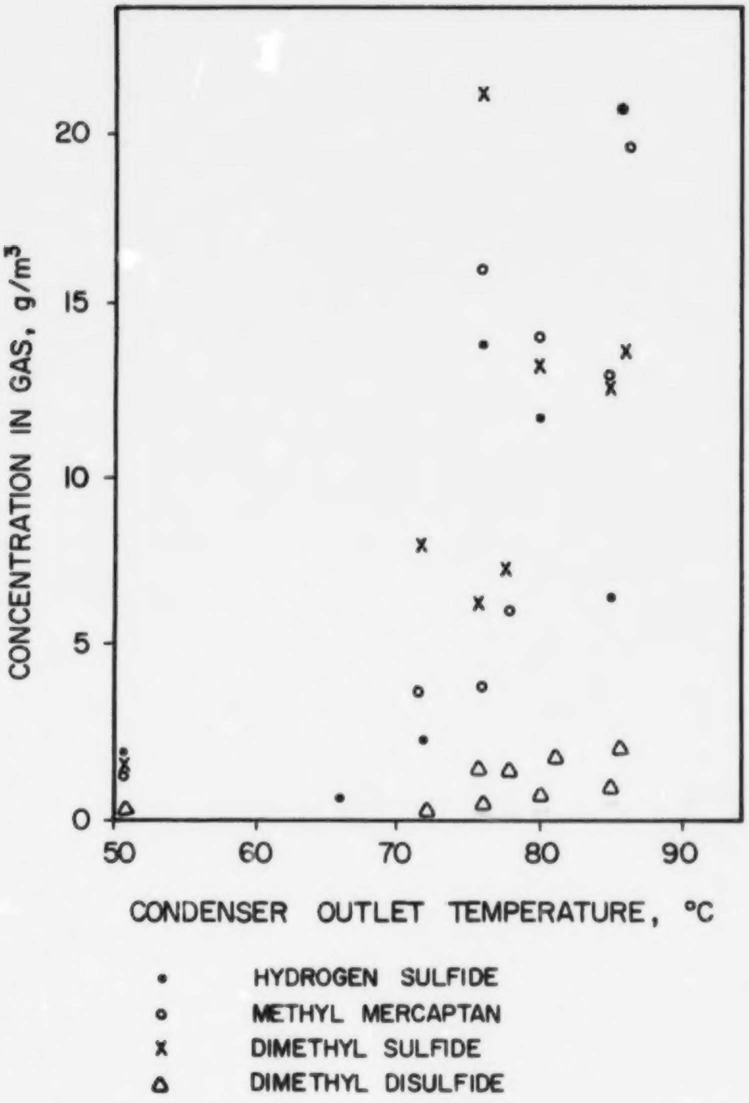


FIGURE 2-7

ODOR COMPOUNDS IN RELIEF GAS AFTER TURPENTINE CONDENSER AS A FUNCTION OF CONDENSER OUTLET TEMPERATURE (2)

The internal construction should consist of adequate baffles to disperse the hot condensate in top layers that are as even as possible. The accumulator should also be evenly insulated to avoid local cold spots where liquid will cool and flow down, mixing the contents of the accumulator.

Experiences from mills show that installed heat exchanger surfaces, which are initially sufficient, may later prove too small. This change occurs because surfaces gradually get fouled, especially on the blow heat side, by fiber and liquor carryover. These dirty surfaces reduce heat transfer and increase pressure drops, thus reducing flows and further decreasing heat transfer. Spiral heat exchangers have an advantage over plate exchangers in decreasing fouling by fiber and liquor carryover, but they are more difficult to clean. Another factor, which will reduce heat transfer, is a reduced hot water demand (flow 5 in Figure 2-1) or a higher warm water temperature (flow 4 in Figure 2-1). Reduced heat transfer means a higher temperature in the accumulator bottom and reduced condensation of the blow gases. Injecting fresh cool water (flow 2 in Figure 2-1) to the primary condenser with controlled temperature counteracts the reduction in condensation. This method is used extensively, but it has the great drawback of increasing substantially the blow condensate bleed (flow 3 in Figure 2-1).

The blow condensate bleed has to be treated, for instance, by steam stripping, and the stripping equipment investment and the stripping steam consumption will directly affect the size of the bleed. Thus, if the blow heat recovery capacity is insufficient, a trade-off between air pollution abatement and water pollution abatement must be made. A successful odor abatement program should include monitoring of temperature and pressure drops over the blow heat recovery heat exchangers to check their performance.

2.1.1.2 Improving Blow Heat Recovery

The most common approach to blow gas treatment is to use a blow gas collection and flow equalization system followed by gas incineration. Any malfunction in the blow heat recovery chain will adversely affect the blow gas treatment, primarily the blow gas collection and flow equalization system, as clearly demonstrated in Figure 2-3.

Mills with odor abatement problems caused by inadequate blow heat recovery can improve their situation by:

1. Improving the blow heat recovery control system through:

    a. More extensive instrumentation of condensing, heat accumulating, and heat exchanging systems, and

    b. Better tuning of the control system.

2. Increasing the blow heat recovery capacity through installation of:

    a. More heat exchanger surface,

    b. More pump capacity for the primary blow steam condenser,

c. More pump capacity for the heat exchanger circulation,

d. Secondary blow-steam condenser,

e. Better baffles in the accumulator, and

f. More accumulator volume.

3. Increasing the flow equalization capacity through installation of more gas (up to 10 times more) accumulator volume.

4. Decreasing the blow heat recovery system load through prolonging the blow period, thereby decreasing pulp production.

An odor control program for the blow heat recovery system should consider recommendation 1, above, first, and then the others. Recommendation 4 should only be used as a last resort.

2.1.2 Relief Gases

The purpose of the digester relief is to remove air and other noncondensable gases during operation and to reduce digester pressure before blowing. Relief takes place more or less continuously during digestion, as well as during the final deliberate blow pressure relief before blowing. For softwood, the amount of steam in the continuous relief is about 180 kg (400 lb), and in the final relief around 90 kg (200 lb) (5). In modern batch digesters, the final blow pressure is more efficiently and swiftly reduced by introducing cooler weak black liquor into the upper part of the digester.

The relief is usually passed through a surface condenser, thus producing hot water. When pulping softwood, the relief condensate will contain turpentine, which is recovered in a separating vessel. The noncondensable relief gases flows and compositions are presented in Table 1-2 and Table 1-3. Hardwood usually produces more relief gas than softwood. A normal softwood value is around 1 m^3 per metric ton of pulp (32 ft^3/ton).

The relief gases do not present a major problem because of the relatively small volume and even flow as compared to blow gases. As with the blow gases, the recommended treatment is incineration (section 4.3).

2.1.3 Turpentine Recovery

Turpentine recovery takes place with turpentine-containing softwoods. Recovery is through gas relief to the turpentine recovery system. Typically about 270 kg steam/t (540 lb/ton) of pulp is relieved to and condensed in the recovery system. The condensate is separated into one turpentine fraction and one underflow of contaminated condensate in the decanter. This condensate is one source of odor in a kraft mill and can be treated by steam stripping (section 5.5).

The amount of odor compounds in the relief gas can be decreased by decreasing the condensate outlet temperature (Figure 2-7), which also produces a lower hot water temperature from the condenser.

Decreasing condenser outlet temperature also means greater safety in collecting and handling relief gases when there is a possibility of contact with air, since lower condensing temperature correspondingly produces less turpentine in the relief gas (Figure 2-8).

2.2 Continuous Digester Gases

Continuous digesters present a much smaller pollution problem than batch digesters because contaminated condensates and odorous gases flow at a regular rate. Treatment capacity can be designed for the mean flow, without the need for peak flow equalization as with batch digesters. Continuous digester odor gases do not differ significantly in composition from batch digester odor gases (see Table 1-3).

The amount of noncondensable gases released from the digester itself varies according to how the flash steam is used (Table 1-2). A rather typical downflow of a continuous digester arrangement is presented in Figure 2-9. Other types of continuous digesters exist, but they do not differ very much with respect to air pollution generation. Some types may have a relief vent from the top of the digester to the turpentine recovery system. Most existing units have a countercurrent wash zone in the bottom of the digester. The wash liquor (flow 17 in Figure 2-9) temperature is 75-80° C (167-176° F). This gives a pulp-liquor (flow 1 in Figure 2-9) temperature of 80-85° C (176-185° F). This so-called "cold blow" produces very minor odor emissions from the blow tank. Thus, the major gaseous odor release from the digester will be the flash steam. This steam can be used and condensed in many different ways yielding noncondensable gases, which may be collected and incinerated. The total amount of flash steam is about 0.8 ton per ton of pulp.

2.2.1 Flash Steam

The spent liquor from the continuous digester is drawn off and expanded, or flashed, usually in two stages. The flash steam from the primary flash tank is usually used to impregnate the chips in the presteaming vessel. The presteaming vessel relief, which contains the noncondensable gases from the primary flash steam and from the presteamed chips, then passes to a turpentine recovery system. The amount of primary flash steam to the presteaming vessel is 0.5-0.6 ton per ton of pulp. The secondary flash steam amount is 0.2-0.3 ton per ton of pulp, and it may be used for various purposes.

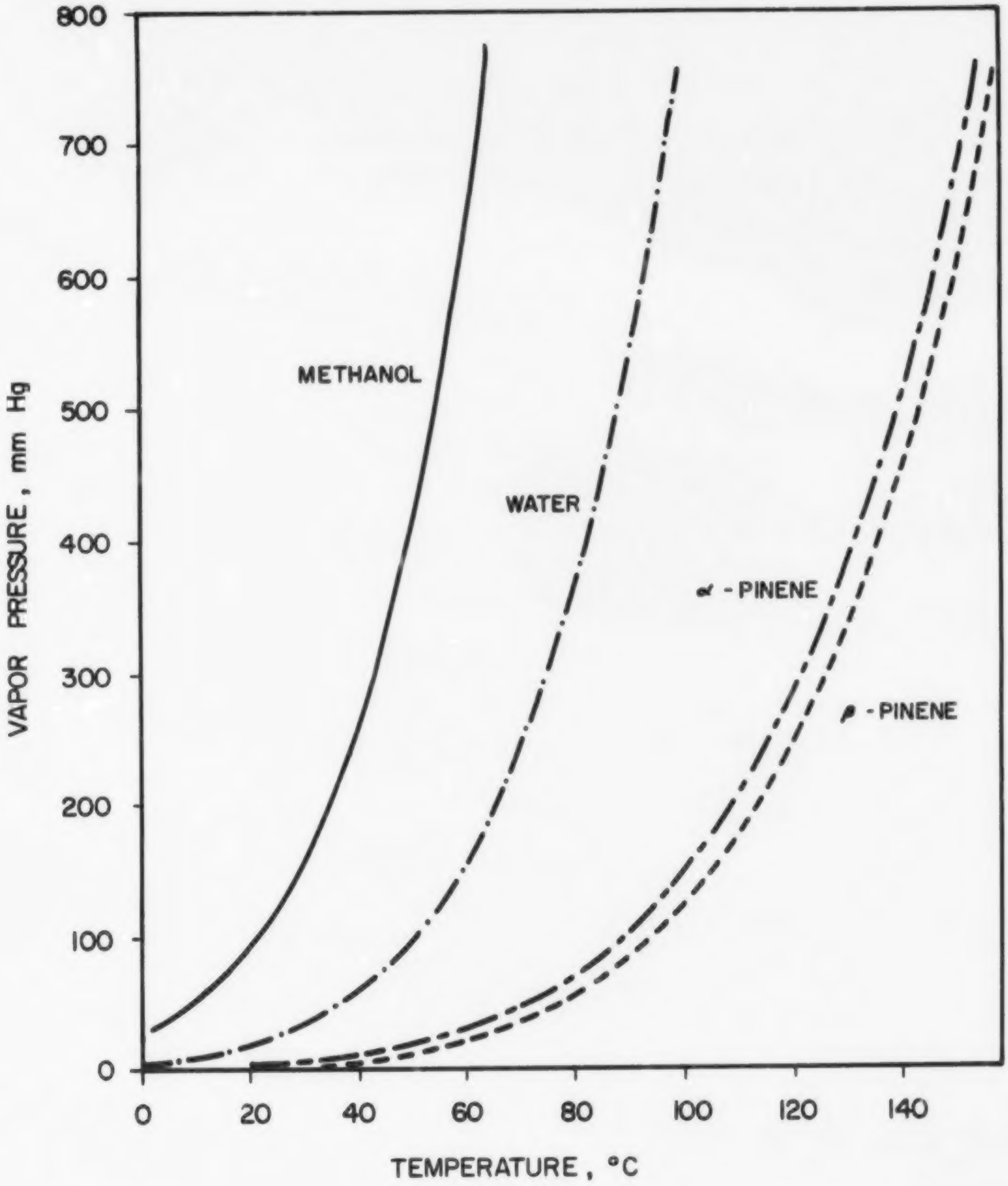


FIGURE 2-8

VAPOR PRESSURES FOR METHANOL, WATER,
α-PINENE & β-PINENE (6)

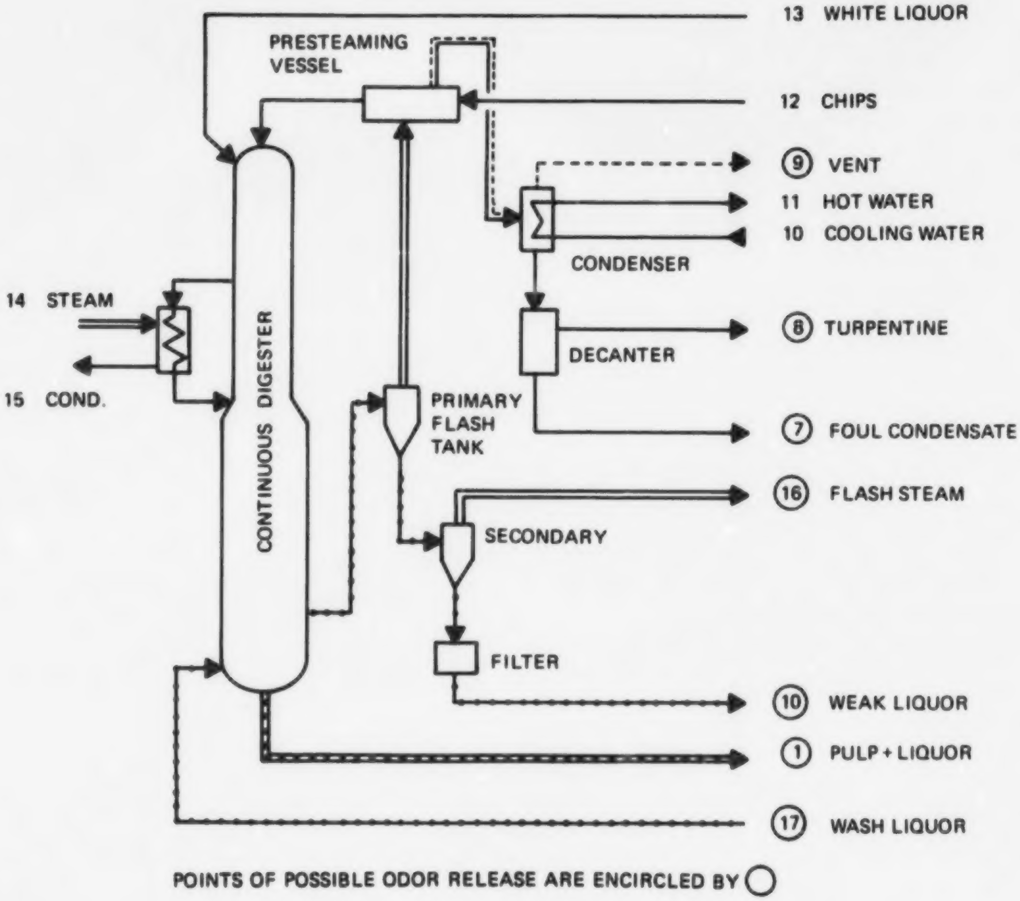

13 WHITE LIQUOR
PRESTEAMING VESSEL
12 CHIPS
⑨ VENT
11 HOT WATER
10 COOLING WATER
CONDENSER
14 STEAM
15 COND.
CONTINUOUS DIGESTER
⑧ TURPENTINE
DECANTER
PRIMARY FLASH TANK
⑦ FOUL CONDENSATE
⑯ FLASH STEAM
SECONDARY
FILTER
⑩ WEAK LIQUOR
① PULP + LIQUOR
⑰ WASH LIQUOR
POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 2-9

CONTINUOUS DIGESTER FLOW SHEET

2.2.1.1 Turpentine Recovery

The relief from the presteaming vessel is brought to a condenser. The amount of condensate is about 0.1 ton per ton of pulp. When pulping soft woods, the condensate is separated in the decanter into a turpentine fraction (flow 8 in Figure 2-9) and an odorous water fraction (flow 7 in Figure 2-9), which is typically treated by steam stripping. The amount and composition of the noncondensable gases (flow 9 in Figure 2-9) varies between values given in Tables 1-2 and 1-3. The amount of odorous compounds can be decreased by decreasing the condenser outlet temperature, as earlier shown in Figure 2-7. The remaining odorous gases may be collected and incinerated (section 4.3). For safety aspects, see section 4.1.3.

2.2.1.2 Flash Heat Recovery

Primary flash heat recovery takes place in the presteaming vessel, as described previously. The secondary flash steam (flow 16 in Figure 2-9) may be utilized in different parts of the kraft mill. Some possibilities are, using it as additional impregnating steam, routing it to the turpentine recovery system (increasing the turpentine and hot water output), condensing it in a separate flash steam condenser for hot water production, using it as a partial steam source for a black-liquor evaporation plant, and using it as a partial steam source for a contaminated condensate steam-stripping column.

Wherever the flash steam is condensed, its noncondensable components will remain and must be collected and treated, preferably by incineration. If treatment does not occur, part of the digester odor is simply transferred to another release point, such as the evaporation plant.

2.3 References

1. Kock, P. A., *Treating Kraft Digester Waste Gases.* M.S. Thesis. Chemical Engineering Department, Helsinki Technical University, Finland. September 12, 1972. (Swedish).

2. Kekki, R., *Kraft Mill Odor Abatement by Condensate Stripping and Waste Gas Incineration.* M.S. Thesis, Wood Industry Department, Helsinki Technical University, Finland. September 18, 1969. (Finnish).

3. Sarkanen, K. V., Hrutifiord, B. F., Johanson, L. N., Gardner, H. S., *Kraft Odor.* Tappi, 53:776-783, May 1970.

4. Martin, G. C., *Fiber Carryover with Blow Tank Exhaust.* Tappi, 52:2360-2362, December 1969.

5. *The Finnish Paper Engineers' Association (SPY).* The Pulping of Wood. Helsinki, Frenckellin Kirjapaino Oy, 1968 (Finnish).

6. Weast, P. C. (ed.), *Handbook of Chemistry and Physics.* 47th edition. Cleveland. The Chemical Rubber Co., 1966. p. D105-D138.

CHAPTER 3

EVAPORATION GASES

The evaporation of black liquor is one of the three major malodorous gas producing processes in a kraft mill; the other two are black liquor combustion and wood digestion.

For the final evaporation of black liquor to combustion strength, there are two different methods in current use. One method is indirect evaporation with steam; the other is direct contact evaporation with hot flue gases from the recovery boiler. This latter method causes an air pollution problem in the combustion of black liquor and is discussed in Chapter 10.

The evaporator gases discussed here are only the noncondensable gases generated from indirect steam evaporation of black liquor. Evaporator gases will contain sulfur and organic compounds boiled off from the black liquor, plus displaced and leaked air.

The amount and composition of the evaporator gases vary widely depending on black liquor properties, such as originating wood, pH, and sulfide concentration, and evaporation plant properties, such as temperature level, equipment type, and plant condition.

The most significant difference between evaporator and digester gases is that the dominating compounds in the evaporator gases are H_2S and CH_3SH instead of organic sulfur compounds. This feature makes odor abatement and sulfur recovery through white liquor scrubbing entirely feasible. Incineration is another possible control technique.

3.1 Black Liquor Properties

The one black liquor property that has the greatest effect on the evaporation plant odor release is its sulfide concentration. Together with pH and temperature, the sulfide concentration determines the quantity of H_2S liberated from black liquor and eventually vented. This relationship is shown in Figure 3-1, which also suggests that a black liquor with a certain sulfidity will generate more H_2S when it has a higher dry solids concentration (i.e., after more evaporation).

Bringing the sulfide concentration down to zero will obviously eliminate the H_2S release from the evaporation plant; this reduction in sulfide concentration also is accomplished by oxidizing the weak, black liquor with air or oxygen before evaporation (see Chapter 9). Black liquor from rotary drum vacuum filters will evolve less odor from diffusion washers, since measurable oxidation of the sulfur content occurs in the filters (3).

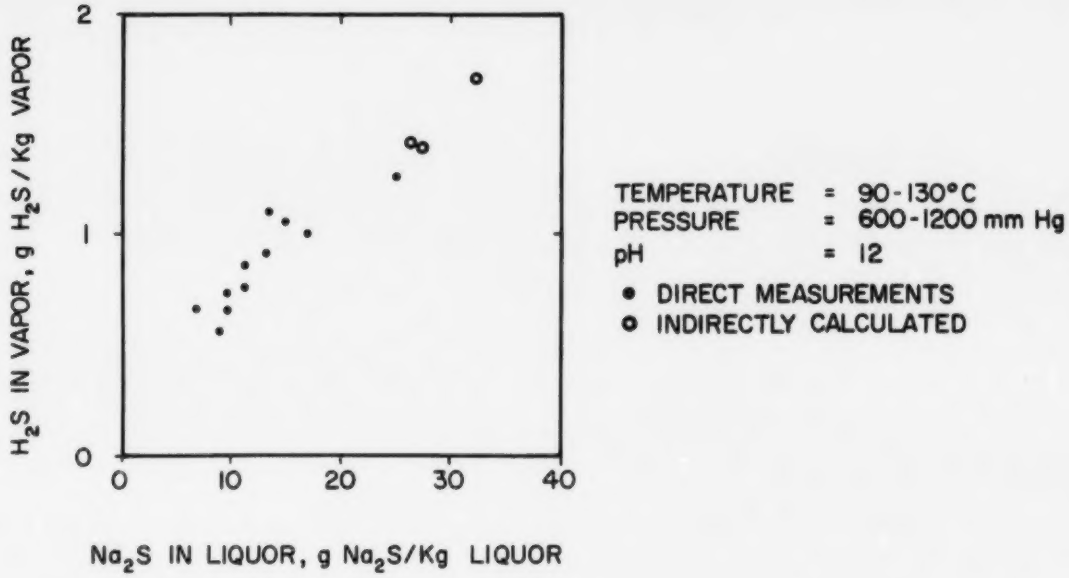


FIGURE 3-1

VAPOR-LIQUOR EQUILIBRIUM FOR H_2S OVER BLACK LIQUOR (1, 2)

The evaporation plant odor release will also depend on black liquor temperatures and pH, but these factors are fixed by process conditions.

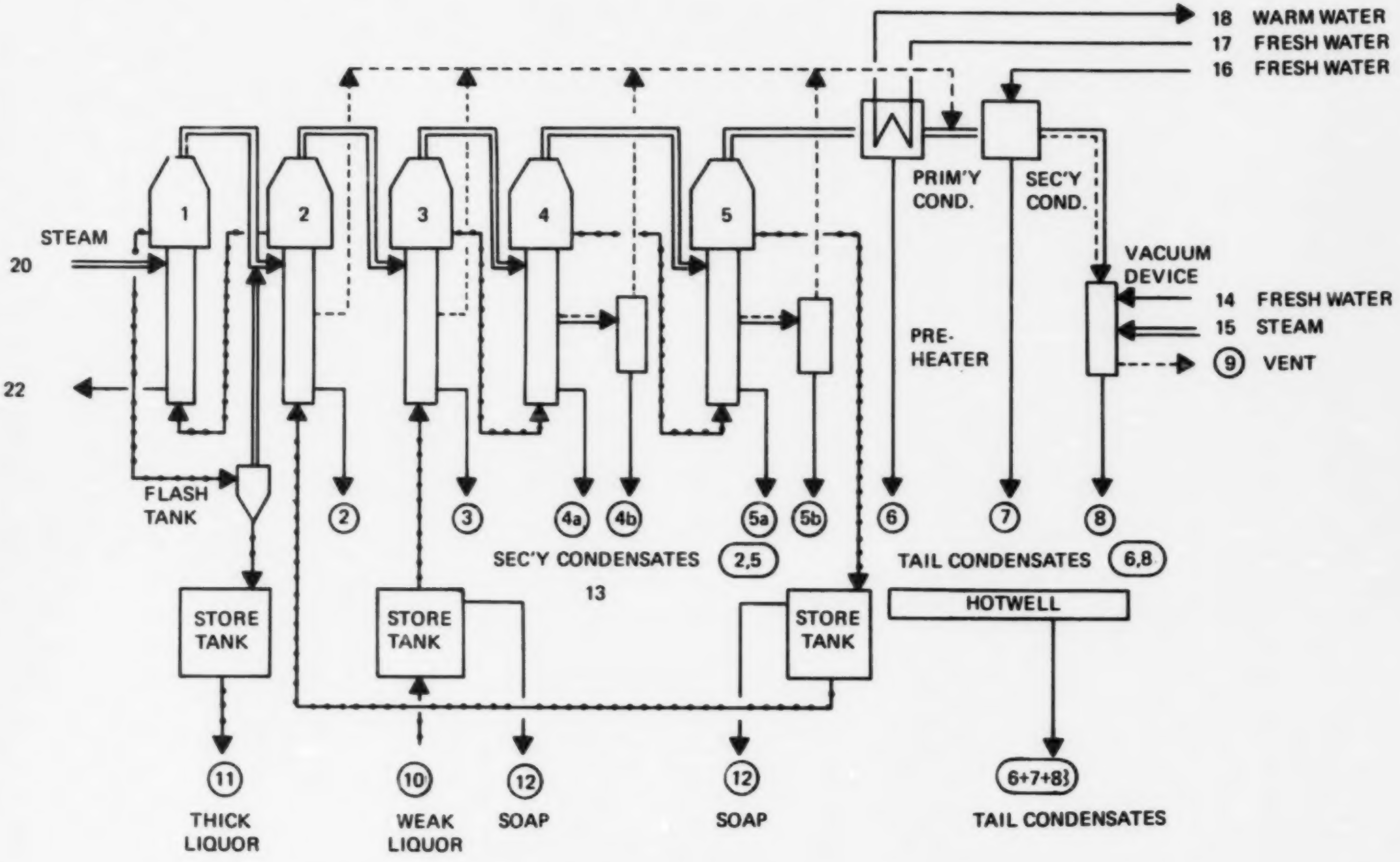
The amount of noncondensable odor gases from the evaporation plant will be greater if the black liquor originates from hardwood digestion than from softwood (3).

3.2 Evaporator Types

There are different ways of evaporating spent black liquor indirectly with steam. The most important ones, from an air pollution point of view, are discussed in the following sections.

3.2.1 Multiple-Effect Vacuum Evaporation

This is the dominant evaporation system. It can have many stages, usually 3 to 7. Each stage may have multiple bodies. It is normally equipped with condensate flashing, liquor preheating, hot water generating, degassing, tail steam condensing and vacuum generating systems. Falling film, rising film, or forced circulation evaporation can be used. The most important features of condensate and gas treatment are shown in a generalized flow sheet in Figure 3-2. The flows of condensate from the different stages are shown separately (flows 2-5 in Figure 3-2) to illustrate condensate treatment (section 5.3.2). Actually, they are flashed in series through stages 3 to 5. Stages 2 to 5 are vented to the vacuum system and stages 4 and 5 are equipped with liquor preheaters that serve as vent vapor condensers. The


18 WARM WATER
17 FRESH WATER
16 FRESH WATER
STEAM
20
22
1
2
3
4
5
PRIM'Y COND.
SEC'Y COND.
VACUUM DEVICE
14 FRESH WATER
15 STEAM
⑨ VENT
PRE-HEATER
FLASH TANK
②
③
④a
④b
⑤a
⑤b
⑥
⑦
⑧
SEC'Y CONDENSATES
2,5
13
TAIL CONDENSATES
6,8
HOTWELL
STORE TANK
STORE TANK
STORE TANK
⑪
THICK LIQUOR
⑩
WEAK LIQUOR
⑫
SOAP
⑫
SOAP
6+7+8
TAIL CONDENSATES

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 3-2

MULTI-EFFECT VACUUM EVAPORATION PLANT FLOW SHEET tail-end condensing systems is shown with a surface primary condenser, a generalized secondary condenser (section 3.2.1.2), and a generalized vacuum device (section 3.2.1.3). There are many different ways of feeding and circulating the liquor, but the one shown is very common.

The odorous evaporator gases are usually released from the vacuum device (flow 9 in figure 3-2) through a duct from the hotwell.

The odorous evaporator condensates are usually released as secondary condensates (flows 2 to 5 in Figure 3-2) and as tail condensates from the hotwell (flows 6 to 8 in Figure 3-2). To some extent, a trade-off is achieved between the release of odorous gas and condensate.

The range of flow and composition of the evaporator gases from the hotwell is given in Tables 1-3 and 1-2, respectively. A discussion of some of the factors that influence the gaseous emission and the condensates from the hotwell follows.

3.2.1.1 Evaporator Effect–Venting

The evaporation plant noncondensables generated in each effect must be vented so that they cannot reduce the condensing heat transfer coefficient nor increase corrosion inside the plant. Venting can be done in several ways, but the two principal systems are single-stage venting and two-stage venting.

Single-stage venting is usually done by bleeding off a certain adjusted amount of vapor from each effect to a central vent duct. In a vacuum evaporation plant, the vent duct usually goes to the secondary condenser, then to the vacuum pump, and the gases are vented out of the system from the hotwell or from the steam jet ejector.

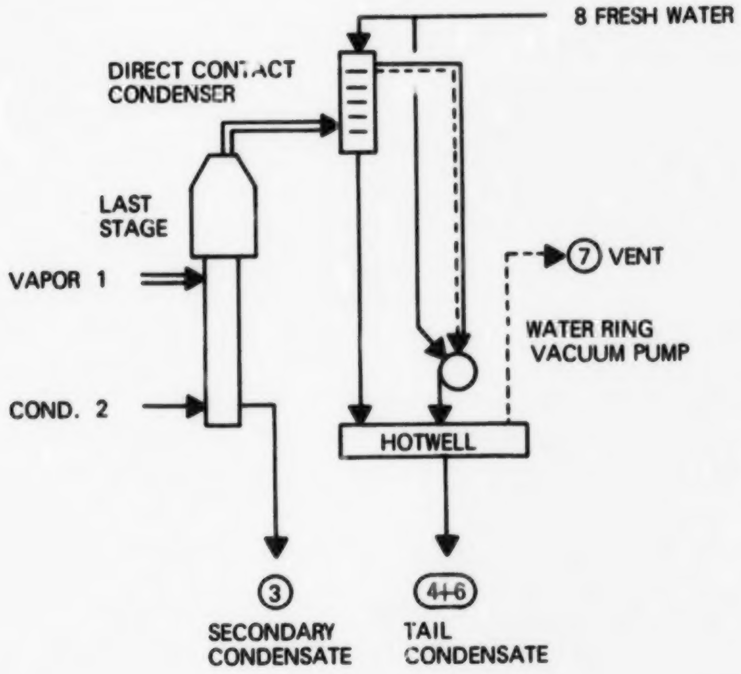
When the weak liquor is fed into the evaporation plant, there is a large boil-off of compounds with high vapor pressure in the feed effect (Number 3 in Figure 3-2). This vapor condenses in the next stage leaving large amounts of noncondensable vapor in that vapor space. Even in the next liquor evaporation stage, boil-off is substantial, and noncondensables are carried over to the following vapor space.

The application of two-stage venting can be advantageous. The vapor spaces of the first one or two stages are vented following the liquor feed stage. These vapor flows amount to 5 to 15 percent of the total vapor flow and are vented to separate condensers. These condensers can serve as preheaters for liquor or water and will, in their turn, be vented to the common duct leading to the vacuum system. In this way the heat transfer coefficients of the evaporator surfaces stay high, and the vapor is condensed in two fractions (for instance, flows 5a and 5b in Figure 3-2). The fraction "a" will be large (say 85 percent of the vapor), but will contain only around 40 percent of the biochemical oxygen demand (BOD) and sulfur compounds. The fraction "b" will be small (about 15 percent of the total), but will contain the remaining 60 percent of the BOD and sulfur compounds. This will greatly facilitate subsequent treatment of the condensates (section 5.3.2).

3.2.1.2 Evaporator Condensers

Evaporator condensers are mainly of two types, surface condensers and direct contact condensers. Both will also be barometric condensers (i.e., they are equipped with barometric legs or tail pipes).

The direct contact condenser, shown in Figure 3-3, is small in size, efficient, hard to plug or foul, and inexpensive. It will, however, add water to the condensates and more noncondensable gases will dissolve in this water depending on the water temperature. Therefore, there is a larger volume of contaminated water to treat at correspondingly larger costs (section 5.3.1). High fresh water temperatures in the summer will require large water


8 FRESH WATER
DIRECT CONTACT CONDENSER
LAST STAGE
VAPOR 1
COND. 2
⑦ VENT
WATER RING VACUUM PUMP
HOTWELL
③
SECONDARY CONDENSATE
(4+6)
TAIL CONDENSATE

POINTS OF POSSIBLE ORDER RELEASE ARE ENCIRCLED BY ○

FIGURE 3-3

EVAPORATION PLANT DIRECT CONTACT CONDENSER WITH WATER RING PUMP flows to maintain sufficiently low pressure in the evaporator plant tail end. On the other hand, there will be less noncondensable gases to treat.

One interesting variation of a water ring pump circuit of an indirectly cooled condenser is one in which white liquor is circulated instead of contaminated condensates. The cooled white liquor scrubs the noncondensable gases and absorbs H_2S and CH_3SH, first in the jet condenser, and then in the water ring vacuum pump. Fresh white liquor is supplied, and the overflow is returned to the process. Using this circuit saves the investment in an entire scrubber (4).

3.2.1.2 Surface Condensers

The surface condenser has some advantages over the direct contact condenser. First, it does not generate more condensate than the vapor condensed. Furthermore, it can be used to produce clean warm water. It is also easier to control. Condensation can be controlled at the desired degree of subcooling of the condensate. Controlled temperature subcooling is used quite efficiently when the condensation is divided between one primary and one secondary surface condenser (Figure 3-4). One can design and dimension the condenser and control the cooling water flows so finely that about 85 percent of the vapor from the last stage will condense in the primary condenser without any subcooling anywhere on the condenser surfaces. Lack of subcooling will allow minimum dissolving of noncondensable gases and low boiling organics in the condensate, and the condensate will be quite low in sulfur and BOD and can be reused without further treatment. The remaining 15 percent of the vapor is sent to the secondary condenser, where it is condensed and subcooled as much as feasible. In this way, a substantial enrichment of noncondensable sulfur compounds and low boiling organics occurs in this condensate, which may then be treated (e.g., by steam stripping). By applying the concept of partial condensation in two steps (section 3.2.1.1), one condensate stream can be divided into a large, rather clean part and a small, highly contaminated part. The small part can be treated at significantly reduced cost. The importance of this design concept will become more evident in the discussion of condensate treatment (see section 5.3.2).

3.2.1.3 Evaporator Vacuum Pumps

Two main types of vacuum devices are in common use, the water ring type of vacuum pump, which is typical in Scandinavian countries, and the steam jet ejector type, which is typical in North America. In some installations other types are used, such as water jet ejector vacuum pumps. All vacuum pumps that allow noncondensable gases to contact fresh cooling water will shift part of the odorous components from the hotwell vent gases to the hotwell condensates.

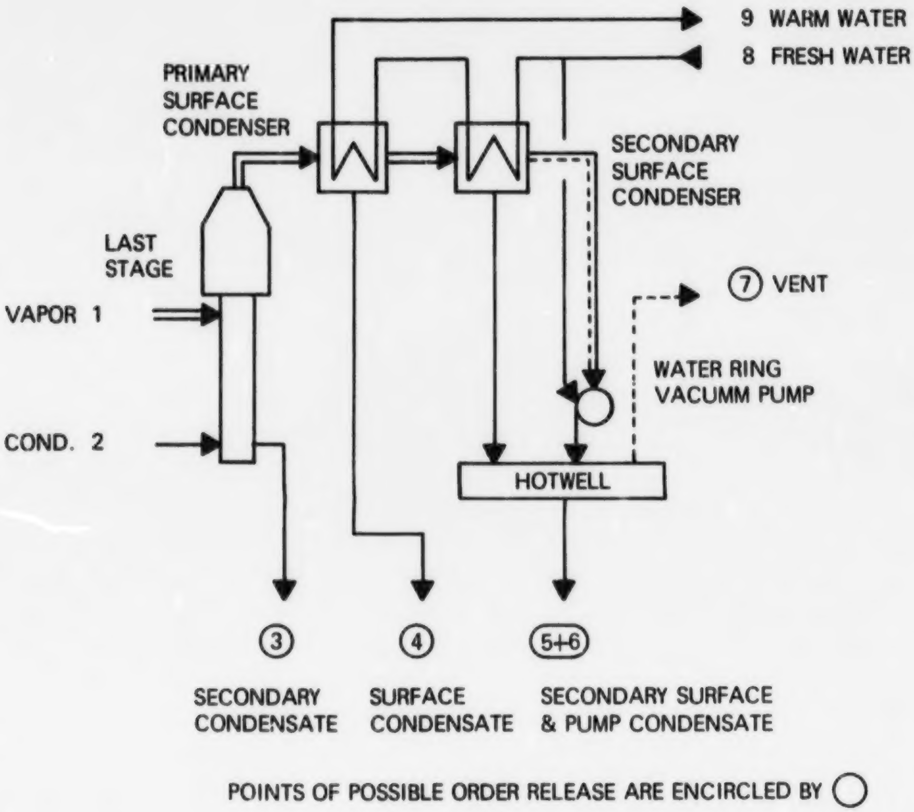

9 WARM WATER
8 FRESH WATER
PRIMARY SURFACE CONDENSER
SECONDARY SURFACE CONDENSER
LAST STAGE
VAPOR 1
COND. 2
⑦ VENT
WATER RING VACUMM PUMP
HOTWELL
③
④
(5+6)
SECONDARY CONDENSATE
SURFACE CONDENSATE
SECONDARY SURFACE & PUMP CONDENSATE
POINTS OF POSSIBLE ORDER RELEASE ARE ENCIRCLED BY ○

FIGURE 3-4

EVAPORATION PLANT TWO STAGE SURFACE CONDENSER WITH WATER RING PUMP

3.2.1.4 Evaporator Flash Steam Feed

One source of primary steam for the evaporation plant is the secondary flash tank of a continuous digester. Depending on the flash steam capacity and its pressure and temperature, it may meet all or part of the steam demand of a particular evaporation plant. In the latter case, it may be supplied to the first evaporator effect or to a alater one. From an air and water pollution point of view, the important thing is that all noncondensable and low boiling compounds flashed from the spend liquor in the flash tank pass over to the evaporation plant and add to the noncondensable gas and contaminated condensate released there. This release will be richer in organic compounds and turpentine than ordinarily is the situation in the evaporation plant. Thus, sulfur recovery with white liquor scrubbing will be less effective, and more caution must be observed when treating the noncondensable gases (sections 4.1.3 and 4.2.3).

3.2.1.5 Condition of the Evaporator

According to Table 1-2, the amount of gases from the hotwell may vary between 0.3 and 12 m^3 per metric ton of pulp (10 and 400 ft^3/ton). A reasonable value for softwood would be around 1 m^3 of noncondensable gases per metric ton of pulp (32 ft^3/ton). If much larger values occur, the vacuum portions of the evaporation plant should be inspected for air leaks.

3.2.2 Other Evaporation Types

3.2.2.1 Multiple-Effect Back Pressure Evaporation Plant

The multiple-effect back pressure system (Figure 3-5) is similar to the vacuum evaporation plant, but uses a higher feed steam and tail steam pressure.

The tail steam is then used in some other process in the mill. Most of the noncondensable gases, both sulfurous and organic, will be carried with the tail steam and vented elsewhere, but can be collected for treatment at that point. The higher pressures in this evaporator stage entail higher temperatures that cause more noncondensables to evaporate and also cause a greater risk of liquor burnout on hot spots. Because of this risk, this type of evaporator is currently not in widespread usage.

3.2.2.2 Flash Evaporation Plant

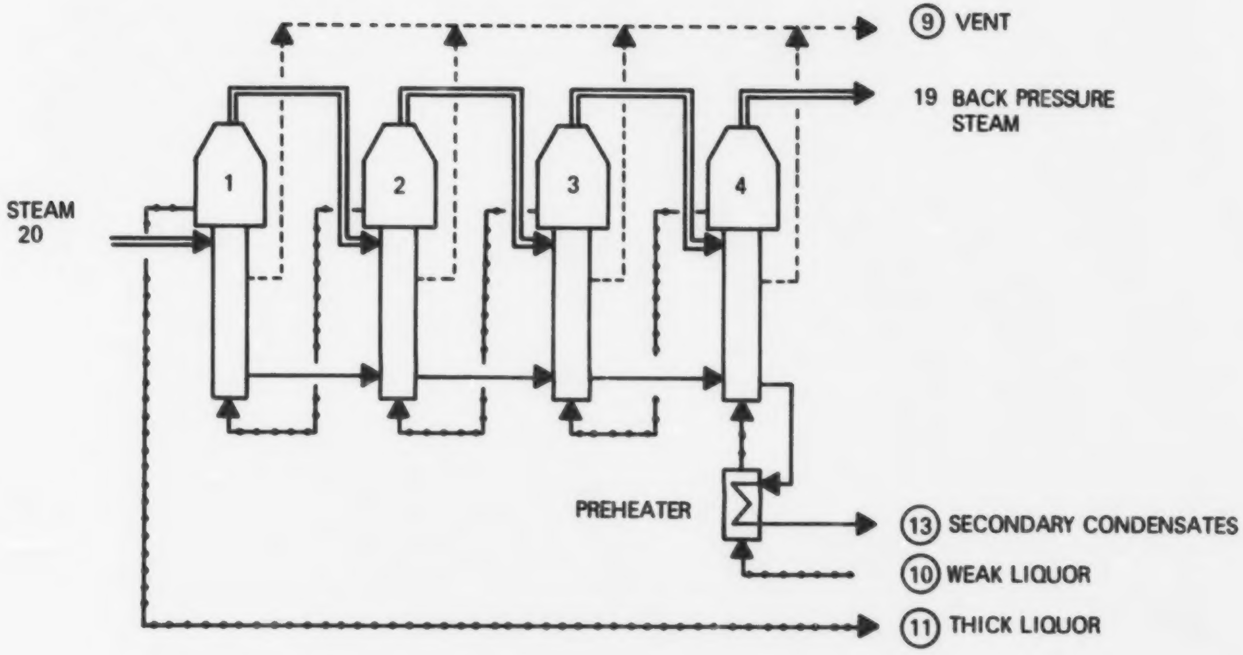
The flash evaporation column (Figure 3-6) is a fairly recent type of evaporator for black liquor evaporation. In the column, the liquor is passed down and flashed in stages under decreasing pressure. The flash steam is used to preheat the liquor in stages on its way up to a new cycle of flashing. The evaporator includes a vacuum condensation system and operates with complete crosscurrent flow. The gases vented from the vacuum system are very similar to those from an ordinary multistage vacuum evaporation plant.

3.2.2.3 Thermocompressor Evaporation Plant

A thermocompressor evaporation plant (Figure 3-7) is a single-stage evaporator with multiple bodies, through which the liquor is passed in stages. Pressures and temperatures are rather uniform over the whole plant, the compressor furnishing the difference of about 15° C (27° F). All stages are vented through a liquor preheater. Vented gases are similar to those of a back-pressure evaporation plant.

3.3 Evaporator Gas Scrubbing

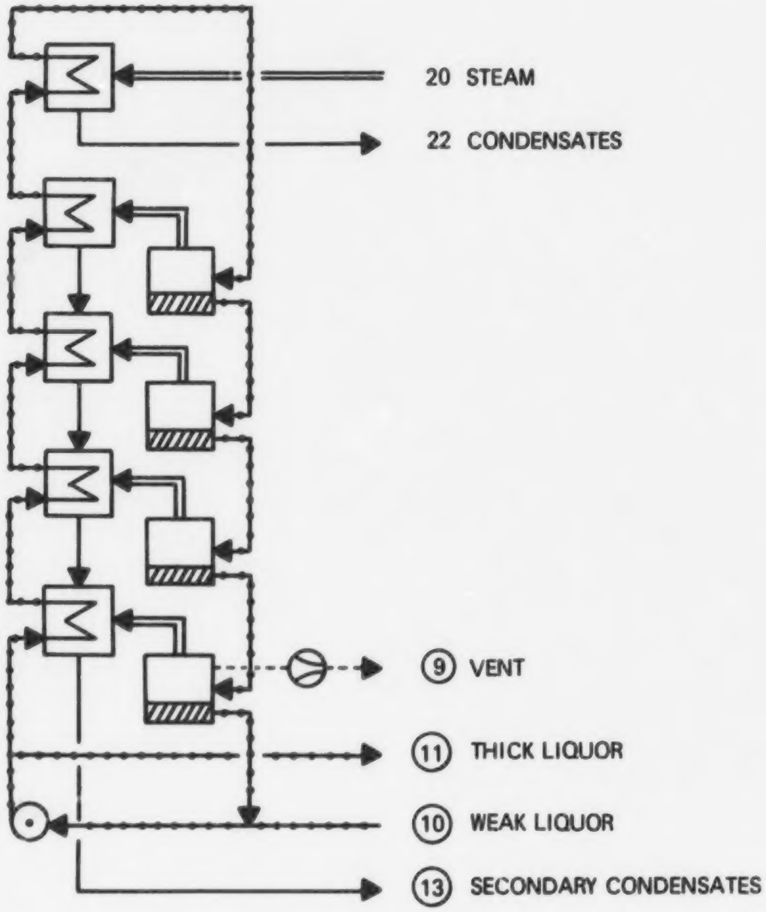
Although noncondensable gas treatment will be extensively reviewed in Chapter 4. evaporator gas scrubbing is discussed here because this equipment can be integrated with the evaporation plant in different ways.


⑨ VENT
19 BACK PRESSURE STEAM
STEAM 20
1
2
3
4
PREHEATER
⑬ SECONDARY CONDENSATES
⑩ WEAK LIQUOR
⑪ THICK LIQUOR

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 3-5

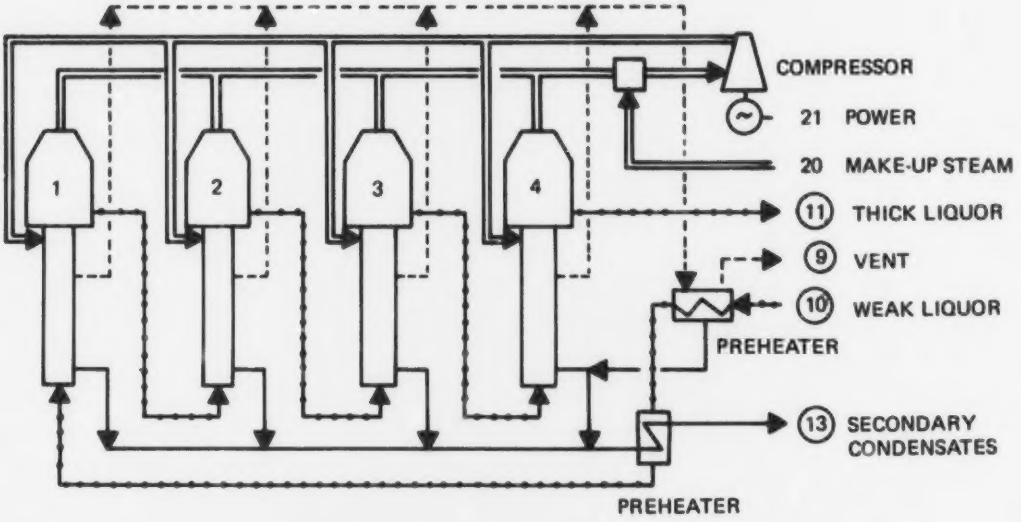
MULTIPLE EFFECT BACK PRESSURE EVAPORATION PLANT FLOW SHEET


20 STEAM
22 CONDENSATES
⑨ VENT
⑪ THICK LIQUOR
⑩ WEAK LIQUOR
⑬ SECONDARY CONDENSATES

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 3-6
FLASH EVAPORATION PLANT FLOW SHEET

Evaporator gas scrubbing with white liquor in a direct contact condenser of vacuum pump was discussed previously (see section 3.2.1.2). It is also possible to install a scrubber after the condenser and before the vacuum pump. The Venemark-design white liquor scrubber has been used in such an application (5). A small scrubber can be installed over the hotwell. Such a scrubber design is shown in Figure 3-8. Noncondensable gases pass through the packed column which is washed with white liquor sprays.



COMPRESSOR
21 POWER
20 MAKE-UP STEAM
⑪ THICK LIQUOR
⑨ VENT
⑩ WEAK LIQUOR
PREHEATER
⑬ SECONDARY CONDENSATES
PREHEATER
1
2
3
4

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 3-7

MULTIPLE EFFECT SINGLE STAGE THERMOCOMPRESSOR EVAPORATION PLANT FLOW SHEET

3.4 General Evaporator Air Pollution Abatement Programs

General programs for abating the air pollution of an evaporation plant include suitable combinations of the following actions:

1. Checking of plant condition, in general, especially for possible leaks;
2. Installing condensers for two-stage venting;
3. Installing surface condensers for two-stage condensing;
4. Collecting contaminated condensates for treatment, such as steam stripping;
5. Installing a direct contact condenser or using vacuum pump scrubbing with white liquor;
6. Installing a suitable white liquor scrubber for hotwell gases;

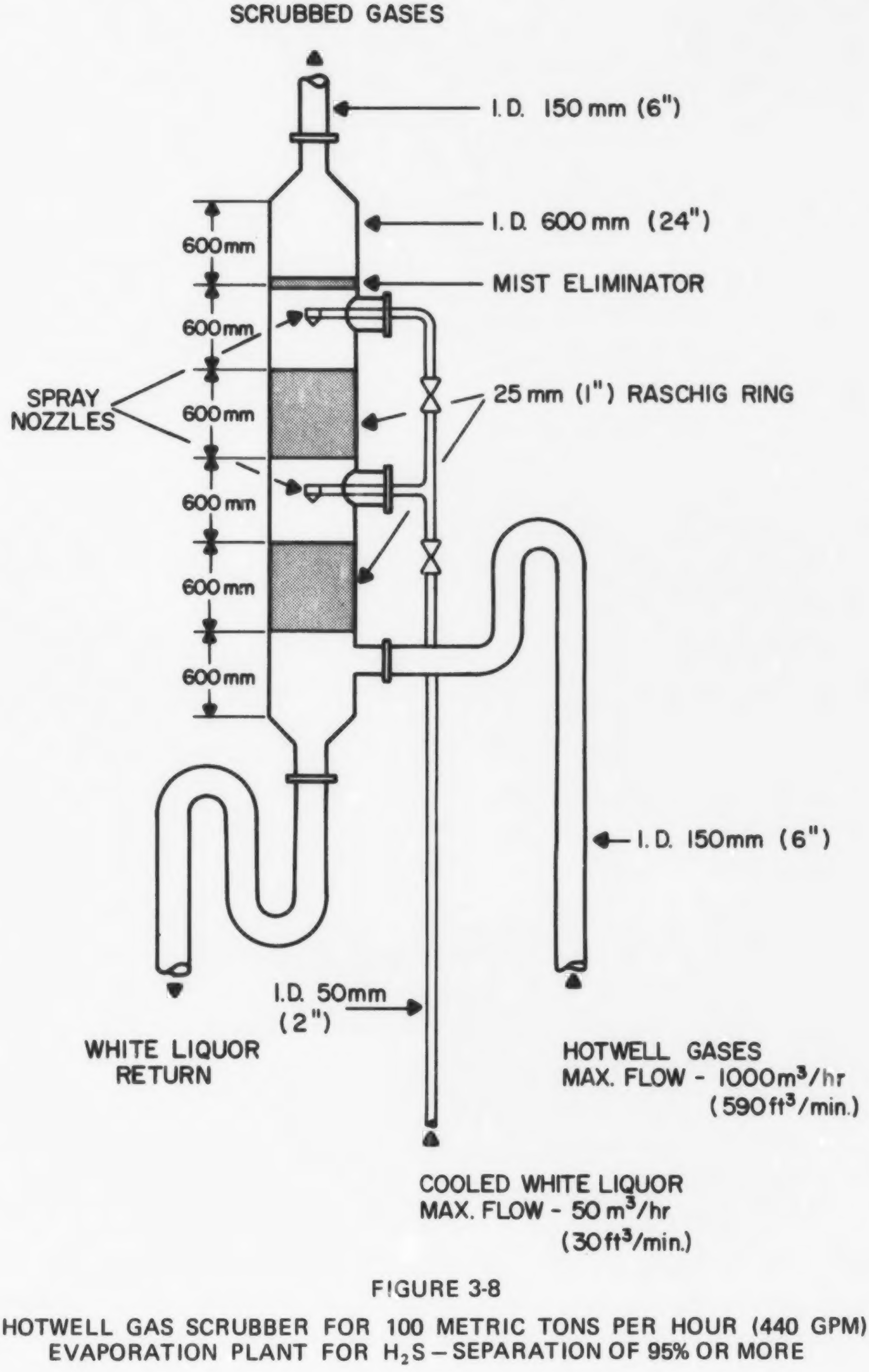

SCRUBBED GASES
I. D. 150 mm (6")
I. D. 600 mm (24")
MIST ELIMINATOR
600mm
600mm
600mm
600mm
600mm
600mm
SPRAY NOZZLES
25 mm (1") RASCHIG RING
I. D. 150mm (6")
I.D. 50mm (2")
WHITE LIQUOR RETURN
HOTWELL GASES
MAX. FLOW - 1000m³/hr
(590ft³/min.)
COOLED WHITE LIQUOR
MAX. FLOW - 50 m³/hr
(30ft³/min.)

FIGURE 3-8

HOTWELL GAS SCRUBBER FOR 100 METRIC TONS PER HOUR (440 GPM) EVAPORATION PLANT FOR H_2S – SEPARATION OF 95% OR MORE

7. Collecting hotwell gases and incinerating them; and

8. Installing a weak black liquor oxidation system.

3.5 In-Plant Controls

Malodorous sulfur gases can be released from black liquor during multiple-effect evaporation by liquor heating and by the stripping action of the steam (6). The H_2S release during multiple-effect evaporation is influenced by the inlet Na_2S concentration, the black liquor pH, and the type and degree of treatment in the weak black liquor upstream of the evaporators (7). The potential liberation of organic sulfur compounds is influenced by their concentration in the incoming black liquor which varies with wood species, the liquor temperature, and the degree and type of treatment upstream of the multiple-effect evaporators.

Major variables upstream of the multiple-effect evaporators which can affect sulfur gas emissions include the wood species pulped, the pulping conditions, the type of pulp washing, and the possible use of weak black liquor oxidation.

The organic sulfur emissions from pulping certain hardwood species are greater than for most softwoods, particularly at high white liquor sulfidity levels. Vacuum drum washing of pulp results in a stripping or organic sulfur compounds and in oxidation of a portion of the Na_2S. Diffusion washing is done in the absence of air and does not involve oxidation of the Na_2S or evolution of the organic sulfur gases. Inlet liquor concentrations of sulfur compounds to the multiple-effect evaporators are expected to be higher following diffusion washing of pulp than following drum washing.

The pH of the black liquor is an important variable affecting the liberation of H_2S and to a lesser extent CH_3SH. Both gases are slightly acidic in nature, with greater ionic dissociation in aqueous solution favored by increased pH. Increasing the black liquor pH above 12.0 helps to reduce H_2S emissions, lignin precipitation as a cause of evaporator plugging, and the tendency for evaporator scaling and corrosion (8) (9). Addition of caustic soda to weak black liquor in controlled quantities can raise the pH to the required levels.

Weak black liquor oxidation with either air or oxygen can reduce sulfur gas emissions from multiple-effect evaporator noncondensable gases. Reid (10) and Galeano (11) report reductions in H_2S emissions of 70 and 99 percent from multiple-effect evaporators after weak black liquor oxidation with air and oxygen, respectively.

Malodorous sulfur compounds emitted from the black liquor during multiple-effect evaporation must end up in either the noncondensable gas stream or the condensate liquid. The type of condenser employed has a definite effect on the distribution of sulfur compounds between these two. Because of its scrubbing action, the use of the barometric jet condenser results in a greater portion of the sulfur compound emissions ending up in the condensate rather than in the gas stream, as shown in Table 3-1 (6).

TABLE 3-1
EFFECT OF CONDENSER TYPE ON REDUCED SULFUR GAS EMISSION FROM EVAPORATOR NONCONDENSABLE GASES (6)*

Condenser Type	H_2S kg S/t	CH_3SH kg S/t	CH_3SCH_3 kg S/t	CH_3SSCH_3 kg S/t	Total kg S/t
Surface	2.28	0.49	0.09	0.21	3.07
Barometric	0.06	0.07	0.05	0.01	0.19
	lb S/ton	lb S/ton	lb S/ton	lb S/ton	lb S/ton
Surface	4.50	0.97	0.18	0.42	6.07
Barometric	0.12	0.13	0.10	0.02	0.37

*kg S/t = kilograms of sulfur per metric ton of air dried pulp
lb S/ton = pounds of sulfur per short ton of air dried pulp

3.6 References

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CHAPTER 4

NONCONDENSABLE GAS TREATMENT

Digester and evaporator noncondensable gases characteristically have relatively low volume flow rates and high malodorous sulfur compounds concentrations. Organic sulfur compounds, such as CH_3SH, CH_3SCH_3, and CH_3SSCH_3, are emitted from digesters in varying quantities from 0.25 to 2.5 kg of sulfur per metric ton of pulp (0.5-5.0 lb sulfur per ton of pulp). The primary sulfur compounds that are emitted from multiple-effect evaporators are H_2S and CH_3SH in quantities ranging from 0.1 to 1.5 kg of sulfur per metric ton of pulp (0.2-3.0 lb sulfur per ton of pulp). Unless properly controlled, these gas streams can cause intense odor pollution at low elevations near the mill.

4.1 Gas Stream Characteristics

The noncondensable gases from digesters and evaporators are relatively high concentration, low volume streams. Their odor levels are easily reduced by chemical or thermal oxidation. Major parameters of the gas stream which must be considered in the design of noncondensable gas handling and treatment systems include temperature, moisture content, flow rate and variability, sulfur gas concentrations, organic material concentrations, and flammability limits.

4.1.1 Process Sources

The major noncondensable gas streams collected and treated in kraft pulp mills are the blow and relief gases from batch and continuous digesters, and the hotwell and condenser vents from multiple-effect evaporators. The gas collection systems for kraft pulp mills must be individually designed to connect all the various gas sources.

Batch digesters normally make up the largest single volume source and give rise to the greatest variations in flow rates of any of the noncondensable gas streams. Batch digesters are normally vented through the relief system at the condenser vent and the turpentine decanter vent. The relief gases are low volume gas streams that flow on a more or less continuous basis during the 3- to 5-hour cooking period. The relief gases normally contain large amounts of terpenes, in addition to the sulfur compounds released during the cook, and can pose an explosion hazard.

The batch digester is normally vented to the blow tank at the end of each kraft cook over a 10- to 20-minute period, with the resultant release of large quantities of steam, inert gas, organic compounds, and malodorous sulfur compounds. The volume of gas released depends on the digester volume, the gas temperature and moisture content, the degree of vapor condensation effected, the amount of air volume in the system, and the amount of inert gases present in the digester. The volume of gas to be handled occurs in a large single surge at the end of each cook. This feature normally requires the use of a flow equalization device to avoid upsetting the operation of the burning device and to assure maximum thermal operating efficiency. The use of sufficiently-sized blow heat condensers may obviate the need for an equalization device.

Continuous digesters normally are nearly constant flow rate devices (except during periods of process upset), requiring no flow equalization devices. Continuous digesters are normally vented at the steaming vessel relief, at both condenser and turpentine decanter vents, from the blow tank vent after the condenser system and sometimes from the top of the digester unit itself. The exact venting system arrangement varies among individual digesters. The total amounts of gas and the terpenes and organic sulfur compounds liberated are not normally as large for continuous as for batch digesters. Also, the amounts are somewhat dependent on the digester blow temperatures. The result is that the point of emission for these materials is often transferred from the digester system to the brown stock washer and multiple-effect evaporator sections.

Noncondensable gases from multiple-effect evaporators differ in character from vent gases from digesters in that they contain smaller amounts of terpenes and organic sulfur compounds. The gases are made up primarily of H_2S and CH_3SH liberated from the black liquor during the evaporation process. Evaporator noncondensable gases are normally collected from the hotwell and condenser vents and can vary between mills. Normally, the noncondensable gas flow rates are considerably larger from indirect contact (surface) condensers than from direct contact (jet) condensers.

4.1.2 Flow Rates

The gas flow rates for individual process streams are subject to wide variations among individual mills, depending on production rate, process operating variables, and the degree of condensation for heat recovery. The single most important flow rate variable for noncondensable gas streams is the peak flow rate for batch digester blow gases, particularly during periods of condenser malfunction. Some type of pressure relief system for batch digester blow gas systems should be provided during periods of condenser malfunction, which are usually indicated by gas temperatures well above normal. A summary of one mill's gas flow rates from a batch digester to a gas holder under conditions of average flow, maximum flow, and condenser upset is presented in Table 4-1.

Major variables affecting the overall gas flow rates from noncondensable gas streams are the process unit type and operating conditions, the production capacity for the particular unit from which the stream is vented, and the degree and type of vapor condensation employed. A summary of typical ranges for noncondensable gas flow rates is presented in Table 4-2.

TABLE 4-1
GAS FLOW RATES FROM A BATCH DIGESTER* (1)**

Operating Condition	Digester Blow Basis		Pulp Production Basis	
	m^3/blow	(ft^3/blow)	m^3/t	(ft^3/ton)
Average	45	(1,600)	4	(128)
Maximum	113	(4,000)	10	(320)
Upset	3,540	(125,000)	320	(10,250)

*Gas flows at actual stack conditions.

**Pulp cooking capacity is 11.4 t/cook (12.6 ton/cook).

TABLE 4-2
TYPICAL RANGES IN DIGESTER AND EVAPORATOR NONCONDENSABLE GAS FLOW RATES

Source	Process Stream	Flow Rate m^3/t (ft^3/ton)
Digester	Batch Blow	475-6,350 (15,200-203,500)
	Batch Relief	0.3-95 (10-3040)
	Continuous	0.6-6 (20-200)
Evaporator	Surface Condenser	0.6-13 (20-420)
	Jet Condenser	0.3-3 (10-100)

Flow rates of noncondensable gas streams to subsequent treatment devices following flow equalization normally range from 5 to 35 m^3/h (3 to 21 cfm) with average values of 10 to 15 m^3/h (6 to 9 cfm) reported (2). Higher flow rates are reported when there is insufficient heat exchanger condensation capacity, when flow equalization is not employed, or when there is significant air leakage into the gas handling system.

4.1.3 Safety Considerations

The design and operation of a system for thermal oxidation of the noncondensable gases require measures to prevent explosions. Four factors that must be considered are variations in gas flow rate, passage of entrained moisture droplets into the burning device, flammability limits of sulfur and organic compounds in the gas stream in the inlet piping, and flame propagation speeds as compared to gas flow velocities in the piping. Of particular importance is the presence of terpene compounds in the noncondensable gas handling and burning systems.

Excessive variations in flow rates of noncondensable gases entering the air inlet of a burning device can blow out the flame. An additional factor which should be considered is that the net retention time of the gas stream in the burning device is reduced during flow surges. Solutions to this problem are to employ large surge tanks with large condenser capacities, to use flow equalization devices, and to provide pressure relief vent systems.

Entrained moisture droplets can create hazards when entering the combustion zone. First, the droplets can cool the flame and may even extinguish it. Second, the evaporation of water can result in a large increase in gas volume as the water changes to steam. These surges in volume can cause an unstable operation in the burning device and lead to a flameout. A flameout may allow an explosive mixture of flammable materials to accumulate in the combustion unit, resulting in an explosion when the system is reignited.

Explosive limits must be considered in the design of noncondensable gas handling systems, both before and after dilution with primary air. A summary of flammability limits for materials commonly present in noncondensable gas streams is listed in Table 4-3 (3).

Terpenes have the lowest explosive limits of any of the compounds listed and are normally the most critical component in noncondensable gas streams for purposes of design for explosive safety.

Work by Ginodman (4), Coleman (5), and DeHaas and Hansen (6) indicates that it is necessary to dilute noncondensable gas streams by a sufficient amount in the primary air inlet before they enter combustion devices. Dilution must occur at a fast enough rate so that the nearly oxygen-free noncondensable gas stream can pass the lower explosive limits of the most critical material (normally terpenes) without an explosion. A summary of the

TABLE 4-3
FLAMMABILITY LIMITS IN AIR FOR COMPOUNDS PRESENT IN KRAFT NONCONDENSABLE GAS STREAM (3)

Material	Flammability Limits Lower	 Upper
	Concentration, % by vol.	
H_2S	4.3	45.0
CH_3SH	3.9	21.8
CH_3SCH_3	2.2	19.7
Terpene	0.8	---

necessary dilution requirements for batch digester relief gas alone, and for combined digester blow and relief gas is presented in Table 4-4.

The primary danger of explosions exists in the primary air inlet of the combustion device immediately following introduction of the noncondensable gases. The presence of large quantities of terpene compounds tends to make digester relief gases a greater explosive hazard than blow gases.

TABLE 4-4
DILUTION REQUIREMENTS WITH AIR TO AVOID EXPLOSIONS FOR DIGESTER NONCONDENSABLE GAS STREAMS (4) (5) (6)

Gas Stream	Volume Dilution Required Air/Gas Ratio
Relief only	50/1
Relief & blow	20/1

An additional consideration regarding potential explosions involves flame propagation speeds of air-gas mixtures. Data collected by Ghisoni (7) on flame propagation speeds for air-mercaptan mixtures are listed in Table 4-5.

TABLE 4-5
FLAME PROPAGATION SPEEDS FOR AIR-MERCAPTAN MIXTURES (7)

Mercaptan Concentration % by Vol.	Flame Velocity m/s (ft/sec)
18.9	0.55 (1.8)
22.8	0.46 (1.5)
23.1	0.40 (1.3)
23.7	0.37 (1.2)
25.5	0.18 (0.6)
25.7	0.15 (0.5)

Gas velocities in the noncondensable gas piping and the primary air inlet must be greater than any flame propagation speeds to prevent damage to process units from possible explosions. Maintenance of gas velocities of at least 1 m/s (3 ft/sec) at all times and the use of flame arrester devices in the noncondensable gas line should minimize the danger of explosions from excessive flame speeds.

4.2 Gas Handling Systems

The major parts of a noncondensable gas handling system are condensation, flow equalization, liquid scrubbing, piping, safety control, and air inlet sections.

Removing moisture and turpentine upstream of the burning device is particularly important in preventing possible flameouts. Sulfur compounds can be absorbed into alkaline liquids for white liquor makeup. The noncondensable gas piping system must be designed with safety devices to prevent explosions and must also have design features to permit the rapid dilution of the noncondensable gas stream before it enters the combustion unit.

4.2.1 Vapor Condensation

The primary purpose of the condensers in digester and evaporator gas handling systems is heat recovery from the gas stream by water vapor condensation.

The condenser systems also remove a portion of the organic vapors, such as terpenes and sulfur compounds. The vapors so removed also require, in turn, treatment of the condensate waters for odor removal. The terpenes can be recovered by flotation and decantation from the condensed water. After collection, they can be sold as byproduct turpentine or used as an auxiliary fuel in the lime kiln.

The condensers also serve to reduce the volume of gas to be treated by cooling the gas stream and thereby condensing out a portion of the contained water vapor. Cooling the gas stream to between 75 and 85° C (167 and 185° F) is normally desirable to remove the major portion of the water and reduce the gas volume. Where no flow equalization devices are employed, the use of large heat transfer surface areas in condensers is particularly important for blow gas streams from batch digesters. Surface condensers are more desirable from a water pollution reduction standpoint than comparable spray or jet condensers since they produce a lower volume of more highly concentrated contaminated condensate. This type of condenser is normally larger in surface area and, therefore, has a higher capital cost.

4.2.2 Flow Equalization

The two major devices employed for noncondensable gas flow equalization are the vaporsphere and the floating cover gas holder. DeHaas and Hansen (6) describe the use of a vaporsphere for collection of batch digester noncondensable gases. The vaporsphere is a spherical device with a flexible fabric diaphragm attached around the epicenter of the sphere as shown in Figure 4-1 (2). The diaphragm consists of a mylar film sandwiched between two layers of cotton canvas that can be fabricated by local tent and awning manufacturers. The useful life of such mylar canvas diaphragms is as long as 27 months (8).

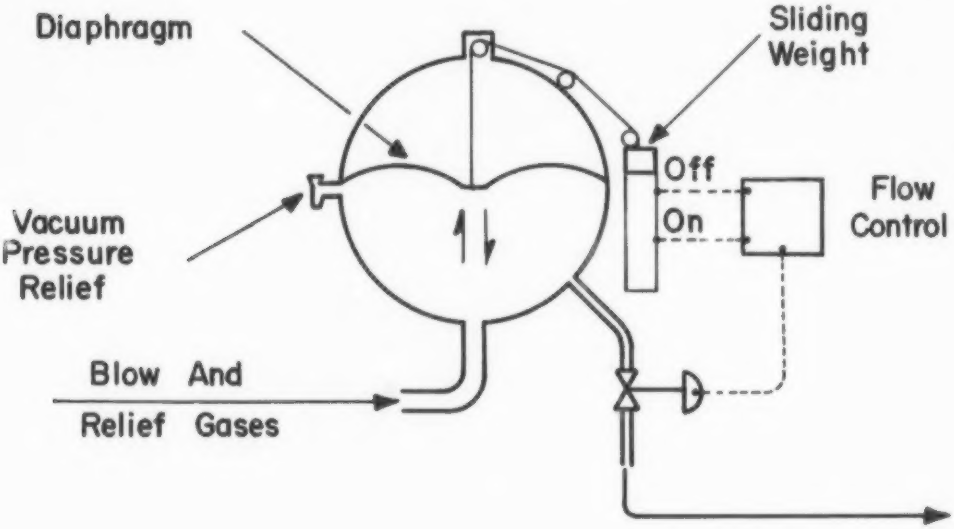


FIGURE 4-1
VAPORSPHERE FLOW EQUALIZATION GAS HOLDERS (2)

Several operating and safety features are necessary to assure safe and reliable operation of the vaporsphere. The system contains a counterweight connected to the diaphragm which moves up and down as the gas flows in and out of the vaporsphere. The diaphragm is weighted to provide a slight positive pressure on the system at all times. Automatic flow controls on the system are used to prevent damage to the diaphragm and to prevent excessive air leakage. A pressure and vacuum relief system prevents damage to the diaphragm from either excessive gas flows from condenser malfunctions or from excessive suctions. The condenser section and all associated piping to the vaporsphere must be sealed to prevent the possibility of air leakage and a potential explosive mixture from forming (6). Also, the inlet and outlet gas streams must be vented separately for the full flow equalization effect to be obtained from the vaporsphere.

Floating cover gas holders also are used for flow equalization in kraft pulp mills. They consist of two vertical cylindrical tanks with the upper located inside the lower and a water seal to prevent gas leakage, as shown in Figure 4-2. Gas enters the inside cover cylinder above the water seal, causing the cover to be displaced upward when gas enters and downward as it exits. Gas is withdrawn from a separate exit pipe to achieve the full degree of flow equalization for the system.

The floating cover gas holder must have several operating and safety features to assure its reliable operation. A pressure and vacuum relief system is added to prevent the shell cylinder from being damaged or dislodged by excessive pressures or vacuums. These are

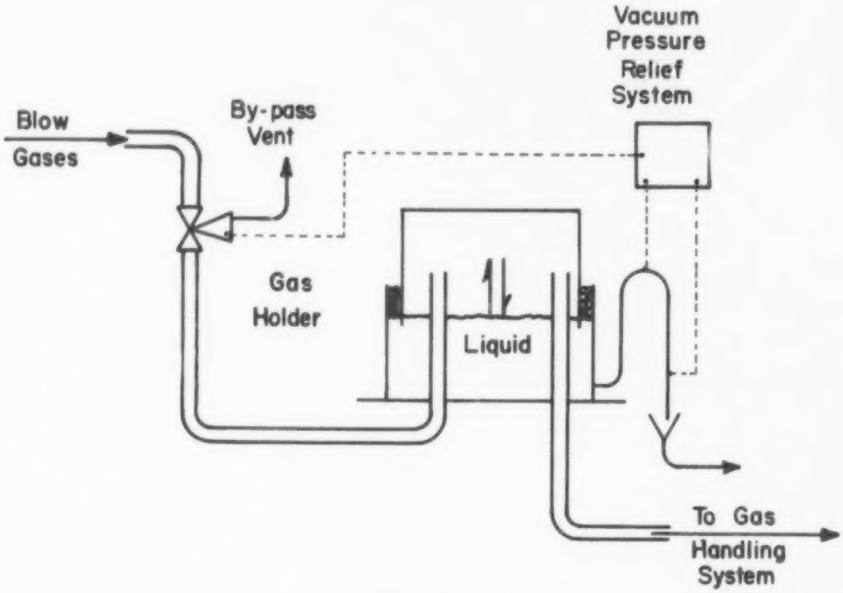


FIGURE 4-2

FLOATING COVER FLOW EQUALIZATION GAS HOLDERS (2) connected to a hydrostatic water seal with an overflow to the drain to prevent the water seal from being lost. A bypass vent allows venting of excessive gas surges such as those caused by condenser malfunctions. Ping pong balls are placed in the space above the water seal between the shell and cover cylinders to maintain alignment and smooth operation.

Vaporsphere and floating cover gas holders can normally be constructed of mild steel. Capital costs for these systems, including all appurtenances, are about $20,000 to $35,000. A summary of the dimensions and construction materials for flow equalization devices is presented in Table 4-6 (2).

TABLE 4-6
DIMENSIONS OF FLOW EQUALIZATION DEVICES* IN KRAFT NONCONDENSABLE GAS HANDLING SYSTEMS (2)

Mill	Type of Unit**	Gas Holding Dimensions					
		Diameter		Height		Volume	
		m	(ft)	m	(ft)	m^3	(cu ft)
A	VS	8.2	(27)	--	--	170	(6,000)
B	VS	8.2	(27)	--	--	170	(6,000)
G	VS	8.2	(27)	--	--	170	(6,000)
H	VS	6.6	(21)	--	--	142	(5,000)
E	FC	8.5	(28)	4.6	(15)	283	(10,000)

*Mild steel used at all five mills as material of construction.
**VS = vaporsphere; FC = floating cover.

Values for digester blow gas design flows for sizing flow equalization devices are reported by Blosser and Cooper (2) and DeHaas and Hansen (6). A summary of digester blow gas volume flows for varying operating conditions is listed in Table 4-7.

4.2.3 Liquid Scrubbing

Liquid scrubbing of the noncondensable gas stream is added for purposes of organic mist removal, gas stream cooling, and sulfur recovery. DeHaas and Hansen (6) report that a liquid scrubber is needed to prevent turpentine mist droplets from reaching the burning device and causing periodic flameouts. The contact of the noncondensable gas stream with sufficiently cool scrubber liquor results in additional cooling of the gas stream, reduces its volume, and removes additional water vapor.

TABLE 4-7
BATCH DIGESTER BLOW GAS FLOW RATES FOR SIZING NONCONDENSABLE GAS FLOW EQUALIZATION DEVICES

Operating Condition	Gas Flow/Digester Blow*		Gas Flow/Unit Production*	
	Average	Range	Average	Range
	m^3/blow (cu ft/blow)		m^3/t (cu ft/ton)	
Normal	42 (1,500)	14-113 (500-4,000)	4 (125)	2-5 (70-160)
Condenser Malfunction	425 (15,000)	285-570 (10,000-20,000)	47 (1,500)	31-62 (1,000-2,000)
No Heat Recovery	1,130 (40,000)	5,660-18,400 (200,000-650,000)	1,250 (40,000)	625-2,000 (20,000-64,000)

*Gas flows are at stack conditions.

The use of alkaline scrubbing liquids, such as sodium hydroxide (NaOH) solution or white liquor, results in removal of the acidic sulfur compounds, such as H_2S and CH_3SH, from the noncondensable gas for return to the chemical makeup system. It is not possible, however, to remove significant quantities of organic sulfur compounds, such as CH_3SCH_3 and CH_3SSCH_3, from the noncondensable gas stream under normal circumstances. Reduced sulfur gas emissions from digester gas sources can range from below 0.25 to above 2.5 kg per metric ton of pulp (0.5 to 5.0 lb per ton of pulp); evaporator noncondensable gas sulfur emissions are normally 0.025 to 0.25 kg per metric ton of pulp (0.05 to 0.5 lb per ton of pulp). Sulfur compounds from the digesters are primarily CH_3SCH_3 and CH_3SSCH_3; while sulfur compounds from the evaporators are primarily H_2S with lesser amounts of CH_3SH.

The alkaline scrubbers generally used are packed bed scrubbers employing a countercurrent flow of liquid and gas. The usual packing for these devices is gravel, stone, or one-inch thick packing rings (2). The liquid solution employed for scrubbing is either caustic soda or white liquor for the return to the chemical makeup system, or water for subsequent discharge to the sewer. A typical scrubber system is illustrated in Figure 4-3 (2).

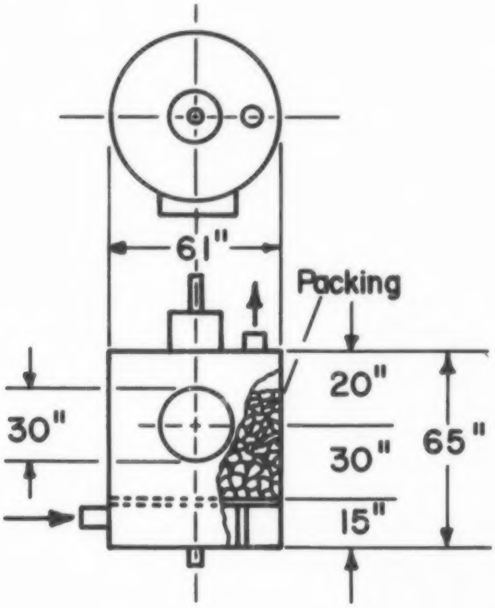


FIGURE 4-3

PACKED BED SCRUBBER FOR NONCONDENSABLE GAS HANDLING SYSTEM

4.2.4 Piping Systems

Design of the piping for a noncondensable gas handling system requires consideration of such items as materials for construction, explosion hazard safety, and gas flow pressure drop. Noncondensable gas handling systems are normally constructed of mild steel, but 304 or 316 stainless steel has been used in some applications to inhibit corrosion. Constructing noncondensable gas piping systems to obtain a minimum velocity of 1 m/s (3 ft/sec) is usually necessary to minimize the likelihood of flame propagation through the pipe. High velocities also result in increased pressure drops through the piping, particularly for lines longer than 30 m (100 ft). An auxiliary fan or a large diameter pipe should be installed to minimize pressure drop across the system and to allow use of the inlet draft of combustion air systems. Most mills have installed 10 cm (4 in) diameter pipe for noncondensable gas piping systems; while 7 cm (3 in) and 20 cm (8 in) have been used in a few mills. The larger diameter piping has found its greatest use at mills employing continuous digesters. A summary of piping system gas velocities, pipe diameters, and materials of construction is presented in Table 4-8.

TABLE 4-8
PIPING SYSTEMS FOR KRAFT NONCONDENSABLE GAS HANDLING SYSTEMS (2)

Mill	Diameter		Gas Velocity		Materials of Construction
	cm	(in)	m/s	(ft/sec)	
A	10	(4)	1.5	(4.8)	Mild steel
B	10	(4)	1.6	(5.3)	Mild steel
C	20	(8)	3	(9.9)	316 Stainless
D	20	(8)	13	(41.7)	304 Stainless
E	10	(4)	1.7	(5.7)	Mild steel
F	10	(4)	–	–	Mild steel
G	20	(8)	7	(23.1)	Mild steel
H	7	(3)	1	(3.3)	Mild steel

4.2.5 Safety Considerations

In designing noncondensable gas handling systems, specific safety features are needed to assure a minimum explosion hazard, prevent liquid entrainment, and assure stable operation of combustion devices. Condensate traps to remove water are placed at low points in the piping system at intervals of approximately 15 m (50 ft) and just upstream of the air inlet. A typical liquid condensate trap design is illustrated in Figure 4-4 (2). The packed bed scrubbers also serve the function of moisture removal to prevent upsets of burner operation,

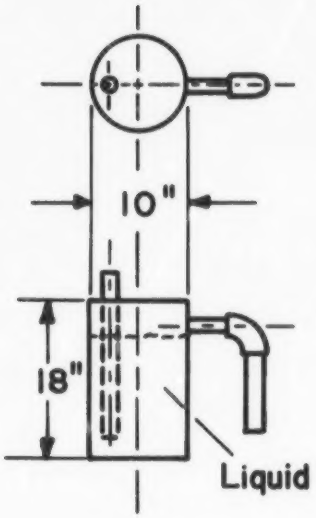


FIGURE 4-4

LIQUID CONDENSATE TRAP FOR NONCONDENSABLE GAS HANDLING SYSTEM

or flameouts, by liquid droplet entry to the combustion zone, and to eliminate false signals to the flameout control.

Flame arresters of the leaf or grid type are commonly added to the noncondensable gas line to prevent the passage of any flame fronts to the process units. The flame arrester normally is added to the noncondensable gas line immediately upstream at the point of introduction to the primary air ducts, as shown in Figure 4-5 (2). One or more additional flame arresters can be installed in long piping systems to gain further protection from possible explosions.

Two features are added to provide emergency venting of excess gas pressures during possible explosions. Rupture discs are added to noncondensable gas lines at approximately 30 m (100 ft) intervals. These devices have diaphragm discs set to explode at certain bursting pressures. To cope with power failures, an emergency vent release is normally placed in the noncondensable line connected to the flameout control for the combustion device. A continuous recording device with input from an orifice meter provides a useful record of system flow rate.

Design for safe confluence of the noncondensable gas stream with the primary air to the combustion device requires consideration of inlet draft, gas velocity, and physical features. A damper is normally placed in the primary air inlet upstream of the point of gas introduction to provide an inlet vacuum of 2.5 to 7.5 cm H_2O (1 to 3 inches of water) necessary to maintain gas flow. Otherwise, an auxiliary fan is needed in the noncondensable gas handling system. The gas is added through a horizontal pipe placed across the primary

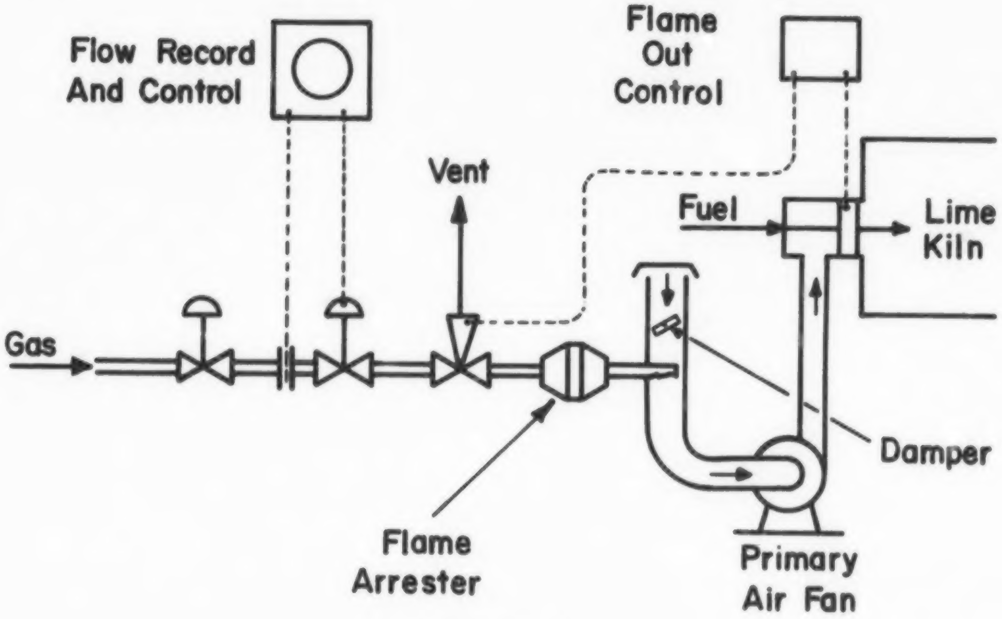


FIGURE 4-5

SAFETY DEVICES FOR NONCONDENSABLE GAS HANDLING SYSTEMS

air duct with holes evenly spaced along the pipe on the downstream side to achieve even distribution and rapid dilution of the gas to well below explosive limits. Gas velocities in the primary air inlet duct after mixing with air are normally above 9m/s (30 ft/sec).

4.3 Gas Treatment Systems

The major techniques for treatment of malodorous sulfur gases to prevent their emission to the atmosphere are thermal oxidation and liquid absorption. The major types of devices for thermal incineration of noncondensable gases are the lime kiln and catalytic furnaces, but limited use is also made of other combustion systems. The liquid solutions employed to date are acidic chlorination bleaching effluent and caustic solutions. Thermal oxidation in lime kilns provides a positive means for destruction of malodorous sulfur gases. Liquid scrubbing can also prove effective as an alternate treatment system or as a pretreatment technique for safety considerations or for sulfur recovery.

4.3.1 Lime Kiln Incineration

Incineration of digester and evaporator noncondensable gases in lime kilns provides a positive method for odor control, without the necessity of constructing an additional combustion unit, and also allows heat recovery. The noncondensable gases normally are added to the primary air inlet of the lime kiln at a dilution of at least 50 to 1 and an air inlet velocity of

at least 9 m/sec (30 ft/sec). A flameout control on the lime kiln is connected to a three-way emergency bypass vent in case of power failure.

Gases are incinerated in the kiln at maximum temperatures of about 1200 to 1400° C (2200 to 2550° F) to achieve complete oxidation of the sulfur compounds present. The SO_2 formed is largely collected by the lime, as calcium sulfite (Ca_2SO_3) instead of being emitted to the atmosphere. To date, mills employing noncondensable gas incineration have not observed any adverse effects on either reburned lime quality or causticizing system operation from the burning of these gases.

The basic layout of the burning system for incinerating noncondensable gases consists of the collection piping and burning sections. Systems where batch digester gases are collected require a flow equalization device or suitably large condenser capacity. The layout for a typical unsteady state system for batch digester blow and relief gases is illustrated in Figure 4-6; a steady state system for a continuous digester is illustrated in Figure 4-7 (2). A combination system for gases from both batch and continuous digesters, plus evaporator gases, is illustrated in Figure 4-8. The noncondensable gas flow rates, their sources, and burning devices employed for eight existing installations are presented in Table 4-9.

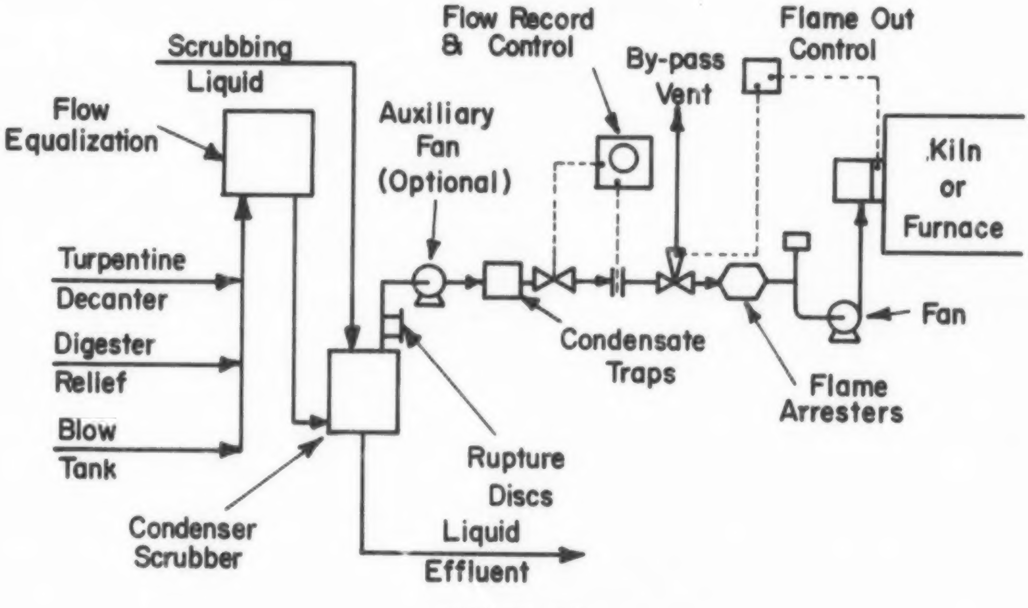

Scrubbing Liquid
Flow Equalization
Flow Record & Control
Auxiliary Fan (Optional)
By-pass Vent
Flame Out Control
Kiln or Furnace
Turpentine Decanter
Digester Relief
Blow Tank
Condensate Traps
Fan
Flame Arresters
Rupture Discs
Condenser Scrubber
Liquid Effluent

FIGURE 4-6

UNSTEADY STATE FLOW SYSTEM FOR BATCH DIGESTER NONCONDENSABLE GAS INCINERATION (2)

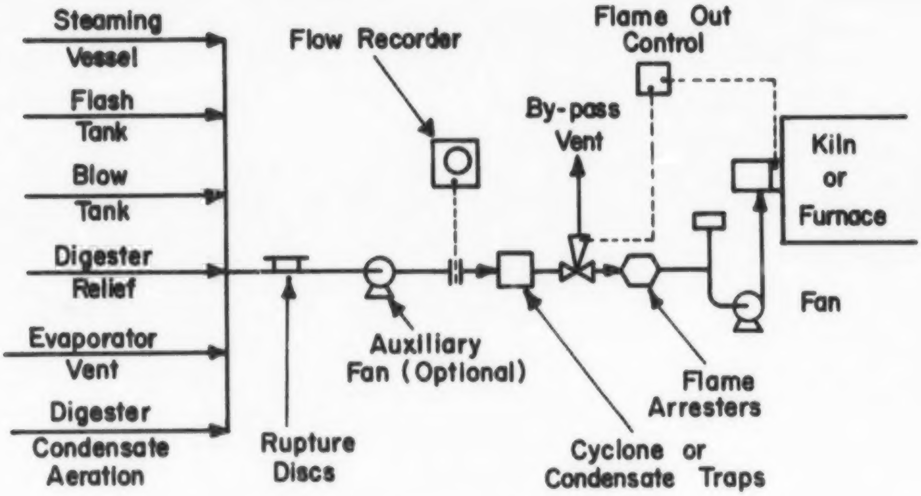

Steaming Vessel
Flash Tank
Blow Tank
Digester Relief
Evaporator Vent
Digester Condensate Aeration
Rupture Discs
Flow Recorder
Auxiliary Fan (Optional)
Flame Out Control
By-pass Vent
Kiln or Furnace
Fan
Flame Arresters
Cyclone or Condensate Traps

FIGURE 4-7

STEADY STATE FLOW SYSTEM FOR CONTINUOUS DIGESTER NONCONDENSABLE GAS INCINERATION (2)

TABLE 4-9
GAS FLOW RATES TO BURNING DEVICES FROM NONCONDENSABLE GAS HANDLING SYSTEMS (2)

Mill	Daily Pulp Production t (ton)/day	Gas Flow Rate* m³/h (cfm)	Sources Included**	Burning Device
A	363 (400)	42 (25)	BD, TD	Lime Kiln
B	999 (1,100)	48 (28)	BD, EH, TD	Lime Kiln
C	499 (550)	357 (210)	CD	Lime Kiln
D	499 (550)	1,490 (875)	CD, CS	Lime Kiln
E	545 (600)	51 (30)	BD, CD, EH	Lime Kiln
F	1,135 (1,250)	-- --	BD, CD, EH	Lime Kiln
G	499 (550)	850 (500)	BD	Cat. Furn.
H	145 (160)	17 (10)	BD	Cat. Furn.

*Reported at stack conditions.

**Source Code:

BD - Batch digester (both blow and relief).
CD - Continuous digester (both [illegible]w and relief).
CS - Condensate stripping.
EH - Evaporator hotwell.
TD - Turpentine decanter.

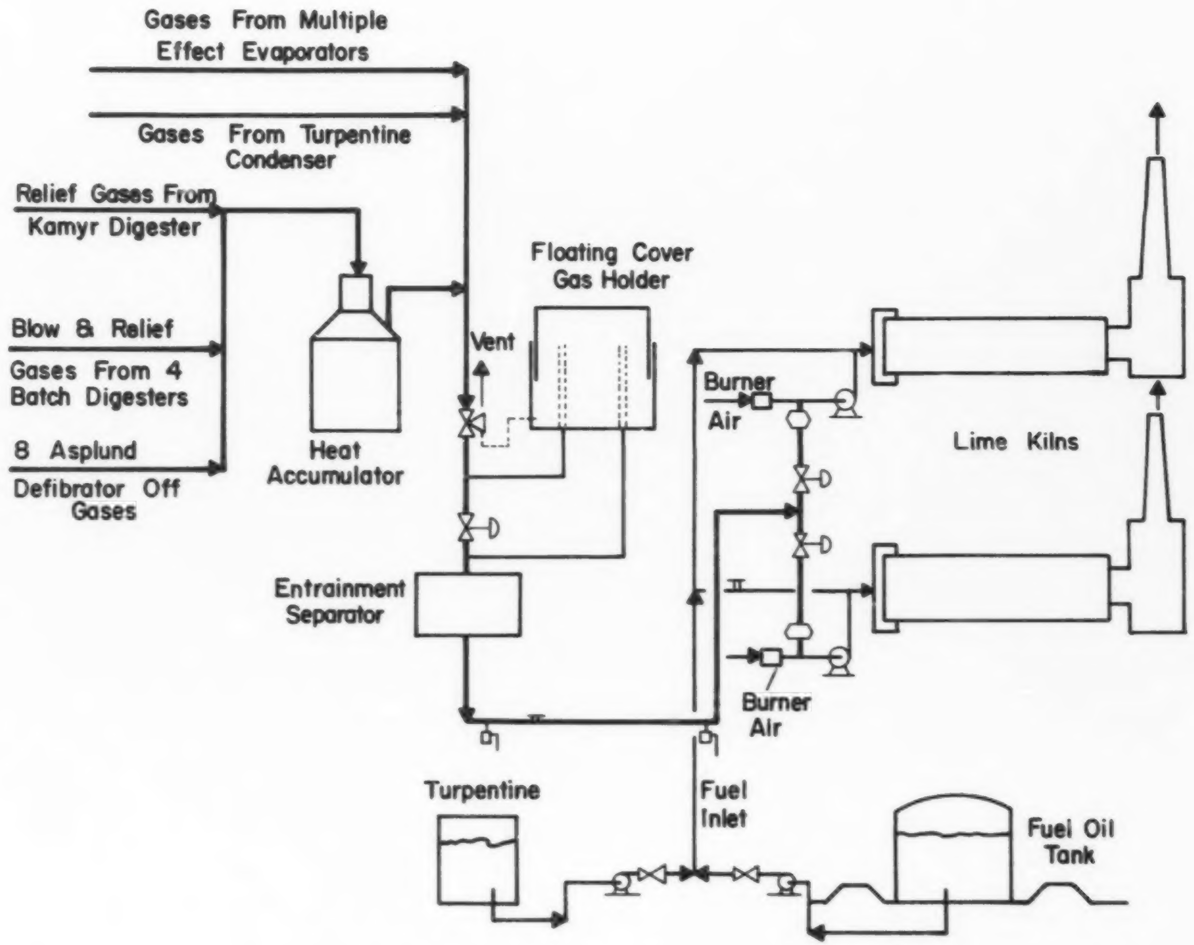

Gases From Multiple Effect Evaporators
Gases From Turpentine Condenser
Relief Gases From Kamyr Digester
Blow & Relief Gases From 4 Batch Digesters
8 Asplund Defibrator Off Gases
Heat Accumulator
Vent
Floating Cover Gas Holder
Entrainment Separator
Burner Air
Burner Air
Lime Kilns
Turpentine
Fuel Inlet
Fuel Oil Tank

FIGURE 4-8

NONCONDENSABLE GAS INCINERATION SYSTEM

4.3.2 Other Incineration Systems

Both catalytic and auxiliary furnaces can be used for incineration of noncondensable gases, but they require a separate combustion unit and the heat cannot normally be recovered. Coleman (5) and DeHaas and Hansen (6) report on the use of an auxiliary furnace for combustion of noncondensable gases. The piping system is the same as for lime kilns. The system burns the gases at 850 to 1000° C (1560 to 1830° F), but does not recover any of the heat produced. The use of the auxiliary furnace has been discontinued because of control maintenance problems and unstable burner operation caused by water and turpentine mist entrainment.

A second installation employs an auxiliary furnace for incineration of batch digester and evaporator noncondensable gases without the use of a flow equalization device. The system employs both blow heat condensers with large heat transfer surface areas and surge tanks of large capacity. Large air dilution is required along with careful gas flow rate control; one explosion with the system did occur (9).

Catalytic furnaces are employed for noncondensable gas incineration at two mills. Noncondensable gases are diluted with air, as in lime kiln systems, and are incinerated at 400° C (750° F) in the presence of porcelain rods coated with an alumina-platinum catalyst. Shortcomings of the systems include incomplete oxidation of organic sulfur compounds, requirements for considerable maintenance of automatic controls, and frequent replacement of the catalyst cells if these are allowed to contact water droplets (2).

Other methods of incineration of incineration of noncondensable gases have been reported. Ghisoni (7) reports on the burning of digester and evaporator noncondensable gases in a natural gas-fired power boiler; Lindberg (10) describes the addition of noncondensable gases to the primary air inlet of a kraft recovery furnace. Adams (11) describes the use of recovery furnaces, auxiliary furnaces, and waste wood burners for incineration of noncondensable gases.

4.3.3 Liquid Scrubbing Systems

The two major types of scrubber liquids employed, to date, are caustic soda and acidic chlorination bleaching effluent. Chase (12) describes the use of alkaline scrubbing to remove H_2S from evaporator noncondensable gases for return to the chemical makeup system. Alkaline solutions do not have any great affinity for nonpolar organic sulfur gases and do not achieve any significant removal of them.

Morrison (13) describes a system where batch digester blow and relief gases are incinerated in a lime kiln. A backup system employs addition of the digester gases to the dropleg of the acidic chlorination bleaching stage when the burning system is not in use. The excess chlorine converts the sulfur compounds to elemental sulfur, sulfonyl chlorides, sulfoxy compounds, and oxidized terpenes. The system appears to oxidize the sulfur compounds sufficiently to prevent their release to the atmosphere.

4.3.4 Standby Systems

The maximum degree of control of non-condensable gases is achieved by providing alternative combustion units for the incineration of these gases. If lime kiln incineration is practiced, the alternative could be routing the gases to a second lime kiln, a boiler or a furnace. Such a system offers the possibility for continued noncondensable gas control during periods when the primary incineration device is out of service.

4.4 System Economics

4.4.1 Capital Costs

The capital costs for a noncondensable gas handling system depend on these parameters:

1. Diameter, length, and materials of piping;
2. Number, type, and size of safety appurtenances; and
3. The possible use of flow equalization gas holders and auxiliary fans.

The flow equalization gas holder is basically a fixed cost item of \$25,000 to \$50,000, based on type and size of unit, and is independent of the amount of pulp production. Piping and safety devices add an additional \$25,000 to \$75,000 or more to the cost of the system. The use of auxiliary furnaces instead of lime kilns increases the cost of the system. A summary of installed capital costs for noncondensable gas handling systems is presented in Table 4-10.

4.4.2 Operating Costs

The major operating cost variables for noncondensable gas handling systems are those for the additional electric power for increased kiln air draft or auxiliary fans, and for system maintenance. Combustion of noncondensable gases in the lime kiln achieves additional fuel savings by reducing oil or gas requirements. In addition, turpentine can be burned in the lime kiln to reduce fuel requirements. Morrison (13) reports system maintenance costs of \$2,100 per year; while fuel savings of \$1,200 result from burning noncondensable gases in the lime kiln. Operating costs for noncondensable gas incineration are estimated to be \$0.01 to \$0.05 per metric ton of pulp produced, with an average of \$0.03 per metric ton (\$0.01 to 0.05 per short ton, avg. \$0.03/short ton).

TABLE 4-10
CAPITAL COSTS FOR INSTALLED NON-CONDENSABLE GAS HANDLING SYSTEMS

Burning Device or System	Installed Capital Cost	
	$/daily t	($/daily ton)
Lime Kiln	110-165	(100-150)
Auxiliary Furnace	165-220	(150-200)
Catalytic Furnace	192-275	(175-250)

4.5 References

1. Personal communication with Mr. Andrew F. Reese, Fibreboard Corporation, Antioch, California, February 1970.
2. Blosser, R. O., and Cooper, H. B. H., *Current Practices in Thermal Oxidation of Noncondensable Gases in the Kraft Industry.* Atmospheric Pollution Technical Bulletin No. 34. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York, November 1967.
3. Perry, J. H. (ed.). *Chemical Engineers Handbook*, 3rd. edition. New York. McGraw-Hill Book Company, 1950. p. 1585-1586.
4. Ginodman, G. M., *Purification of Waste Streams from Sulfate Cellulose Manufacture.* Bumazhnaya Promyshlennost, (Moscow) 22 (7):16-22, November-December 1947.
5. Coleman, A. A., *The Combustion of Noncondensable Blow and Relief Gases in the Lime Kiln.* Tappi, 41:166A-168A, October 1958.
6. DeHaas, G. G., and Hansen, G. A., *The Abatement of Kraft Mill Odors by Burning.* Tappi, 38:732-738, December 1955.
7. Ghisoni, P., *Elimination of Odors in a Sulfate Pulp Mill.* Tappi, 37:201-205, May 1955.
8. Hansen, G. A., *Odor and Fallout Control in a Kraft Pulp Mill.* Journal of Air Pollution Control Association, 12:409-412, September 1962.

9. Personal communication with Mr. Dwayne J. Clark, Simpson Lee Paper Company, Everett, Washington, 1972.

10. Lindberg, S., *How One Swedish Mill Destroys Air and Water Pollutants.* Pulp and Paper, 41 (3):35-39, January 16, 1967.

11. Adams, D. F., *A Survey of European Kraft Mill Odor Reduction Systems.* Tappi. 48:83A-85A, May 1965.

12. Chase, S. J., *Control of Air Pollution at the Champion Paper and Fibre Company.* (Paper Read to the Semi-Annual Technical Meeting of the Air Pollution Control Association, Houston, December 3, 1956.)

13. Morrison, J. L., *Collection and Combustion of Noncondensable Digester and Evaporator Gases.* Tappi, 52:2300-2301, December 1969.

CHAPTER 5

CONDENSATE TREATMENT

Besides noncondensable air polluting gases the kraft process produces condensates that are contaminated with different compounds. These compounds can generate both air and water pollution.

A general course of action is to decrease the amount of condensates, collect them, and reuse them; if they are not reusable, the procedure then is to strip them of their contaminating compounds and oxidize these compounds to less harmful forms.

5.1 Condensate Components

The kraft process produces two main condensates, namely digester and evaporator condensates. Both contain compounds that fall into two broad classes:

1. BOD producing compounds that mainly generate water pollution, and

2. Odorous compounds that mainly generate air pollution.

Characteristically, the first class of compounds are volatile (boiling points between 56 and 150° C (133 and 302° F)), chemical oxygen demanding, and partly toxic (turpentine). Typical of the second class of compounds is that they are volatile (boiling points -59 to 117° C (-75 to 243° F)), reduced sulfur containing, odorous, chemical oxygen demanding, and toxic.

Although this section of the manual focuses chiefly on the second class, the odorous compounds, it is advantageous and sometimes necessary to briefly touch upon the first class, the BOD compounds. They may be treated with the same methods, keeping in mind that they are less volatile than the odorous substances.

The main components of typical kraft mill contaminated condensates are enumerated in Table 5-1.

Components 1 to 3, especially CH_3OH, are mainly responsible for the BOD load of the condensates; components 4 to 8 are mainly responsible for the toxicity of the condensates; and components 5 to 8 are mainly responsible for the odor of the condensates. Because of the entrained black liquor, the condensates are, for the most part, on the alkaline side. All these components will exist in kraft mill condensates in varying amounts depending on place of origin (digester or evaporator), pulp raw material (wood species), operating practices

TABLE 5-1
MAIN COMPONENTS OF TYPICAL KRAFT MILL CONDENSATES (1, 2, 3)

No.	Component	Boiling Point		BOD	Sulfur	Odor Threshold
		°C	(°F)	kg/kg	%	ppb
1	CH_3OH	64.7	(148.5)	1.00	0	100,000
2	CH_3CH_2OH	78.5	(173.3)	1.23	0	10,000
3	CH_2COCH_3	56.5	(133.7)	0.67	0	100,000
4	Turpentine (Pinene)	154	(309)	---	0	---
5	H_2S	-59.6	(-75)	0.60	94	0.4-5
6	CH_3SH	7.6	(45.7)	0.07	67	0.4-3
7	CH_3SCH_3	37.5	(99.5)	0.31	52	1-10
8	CH_3SSCH_3	117	(243)	0.61	68	2-20

(such as sulfidity and cooking time), type of equipment (continuous or discontinuous), and condition of equipment (such as capacity and age).

Because of the difficulty in separating air and water pollution aspects of condensate treatment, both are covered together.

5.2 Digester Condensates

Digester condensates will vary in flow and composition. The quantities of condensates are especially different for batch digesters and for continuous digesters.

5.2.1 Batch Digester Condensates

The amount of turpentine decanter condensates from batch digesters is fairly similar in different mills. The condensates may vary depending on digester pressure relief method. A typical composition is given in Table 5-2 and flow and load range in Table 5-3.

The amount of batch digester blow condensates, or the overflow or bleed from the blow heat accumulator (flow 3 in Figure 2-1) is heavily dependent on the amount of additional fresh water (flow 2 in Figure 2-1) that is injected into the condenser (blow steam, direct contact) to boost vapor condensation (section 2.1.1.1). Additional water means more condensate to treat. The importance of a properly dimensioned and efficiently working blow heat recovery system is again emphasized.

TABLE 5-2
TYPICAL KRAFT MILL CONDENSATE COMPOSITIONS, MEAN VALUES FOR 10 MILLS (2)

Condensate Compound	Turpentine Decanter mg/l	Means: Digester Blow mg/l	Evaporator Effects mg/l	Evaporator Hotwell mg/l
H_2S	90	60	40	100
CH_3SH	250	80	10	40
CH_3SCH_3	400	70	5	7
CH_3SSCH_3	130	50	5	15
Total S	550	180	51	135
CH_3OH	6.500	4.300	10,000	1,000
CH_3CH_2OH	1,600	500	60	40
CH_3COCH_3	160	40	6	10
Total BOD	860	490	1,070	1,060

The volume of blow condensates will diminish if the blow heat recovery system works without heat exchanging (i.e., if the direct contact condenser is fed with cool or warm water from the outside and the hot contaminated water in the blow heat accumulator is used directly for pulp washing. Such a system, however, increases the odors from the pulp in the washing area. This pulp will require bleaching. Therefore, such a system will probably not meet future air pollution requirements.

5.2.2 Continuous Digester Condensates

The continuous digester relief and flash condensates are rather similar in composition to the corresponding condensates from batch digesters.

The continuous digester flash condensate will be found in different parts of the kraft mill, depending on where the flash steam is used. Usually the black liquor from the continuous digester is expanded or flashed in two stages, and the steam from the primary flash tank is used in the presteaming vessel (Figure 2-9). Most of the noncondensable and low boiling compounds end up in the turpentine recovery system and are vented from that system. The secondary flash steam may be put into the presteaming vessel, into a condenser for hot water generation, or into an evaporation plant as primary steam (section 3.2.1.4). Consequently, the flash condensates will end up in those places, perhaps mixed with other condensates. Large variations in the amounts of flash and turpentine condensates actually emanating from the digester area will consequently occur.

TABLE 5-3
TYPICAL KRAFT MILL CONDENSATE CHARACTERISTICS FOR 17 MILLS (4)

	Condensates			
Characteristic	Terpentine Decanter	Digester Blow	Evaporator Effects	Evaporator Hotwell
Flow, m^3/t (gal/ton)				
Max.	0.3 (72)	4 (960)	6 (1,440)	16 (3,840)
Mean	0.15 (36)	2 (480)*	6 (1,440)	7 (1,680)*
Min.	0.08 (19)	0.9 (216)	6 (1,440)	1.5 (360)
Sulfur, kg/t (lb/ton)				
Max.	0.08 (0.16)	0.72 (1.44)	2.25 (4.5)**	-- --
Mean	0.05 (0.10)	0.36 (0.72)	0.30 (0.6)	0.60 (1.2)
Min.	0.01 (0.20)	0.10 (0.20)	0.10 (0.2)**	-- --
BOD_7, kg/t (lb/ton)				
Max.	5 (10)***	-- --	15 (30)**	-- --
Mean	1 (2)	2 (4)	6.5 (13)	3.5 (7)
Min.	1 (1)***	-- --	5 (10)**	-- --

*Values exceeding 1 m^3/t (240 gal/ton) pulp indicate fresh water addition to blow heat recovery system or condensing system.

**Includes evaporator hotwells.

***Includes digester blow.

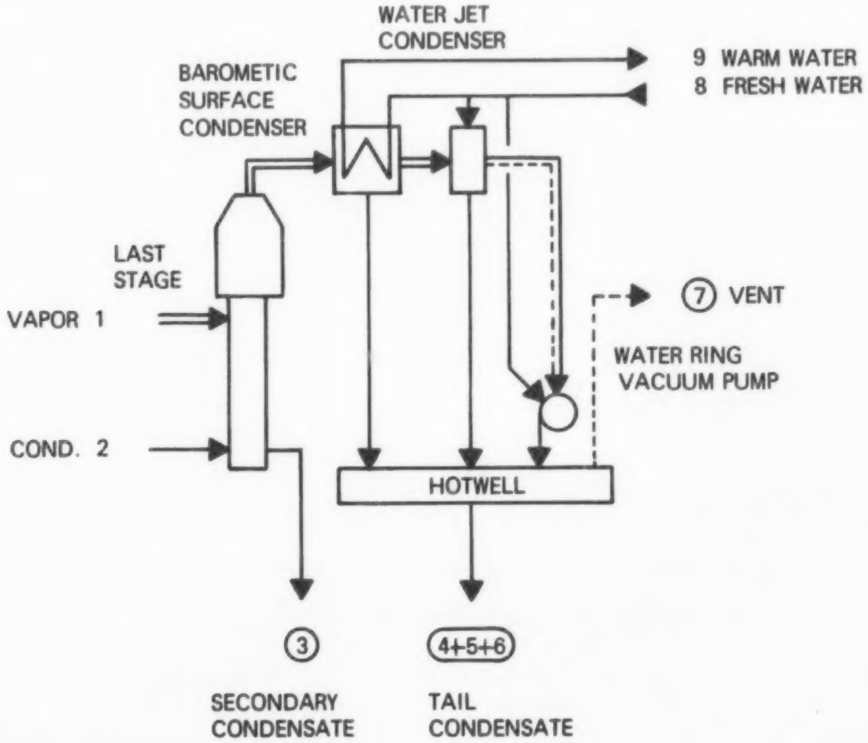
5.3 Evaporator Condensates

The evaporation plant condensates are usually divided into primary condensates emanating from the first stage, secondary condensates emanating from the other stages, and hotwell condensates. The hotwell condensates include condensates from primary and secondary condensers and from the vacuum pulp (refer to Figure 3-2). If the primary steam is pure back pressure steam, the primary condensates are clean (with no leaks) and may be returned to the power station feedwater system.

If the primary steam is wholly or partly flash steam the primary condensate will be contaminated and need treatment. The hotwell condensates will be usually more contaminated than the secondary condensates. Fairly typical values for composition and amounts of the different condensates are given in Tables 5-2 and 5-3. The composition of the condensates varies greatly depending on wood species cooked, sulfidity, evaporation temperatures, and condensers.

5.3.1 Evaporator Condensate Quantity Reduction

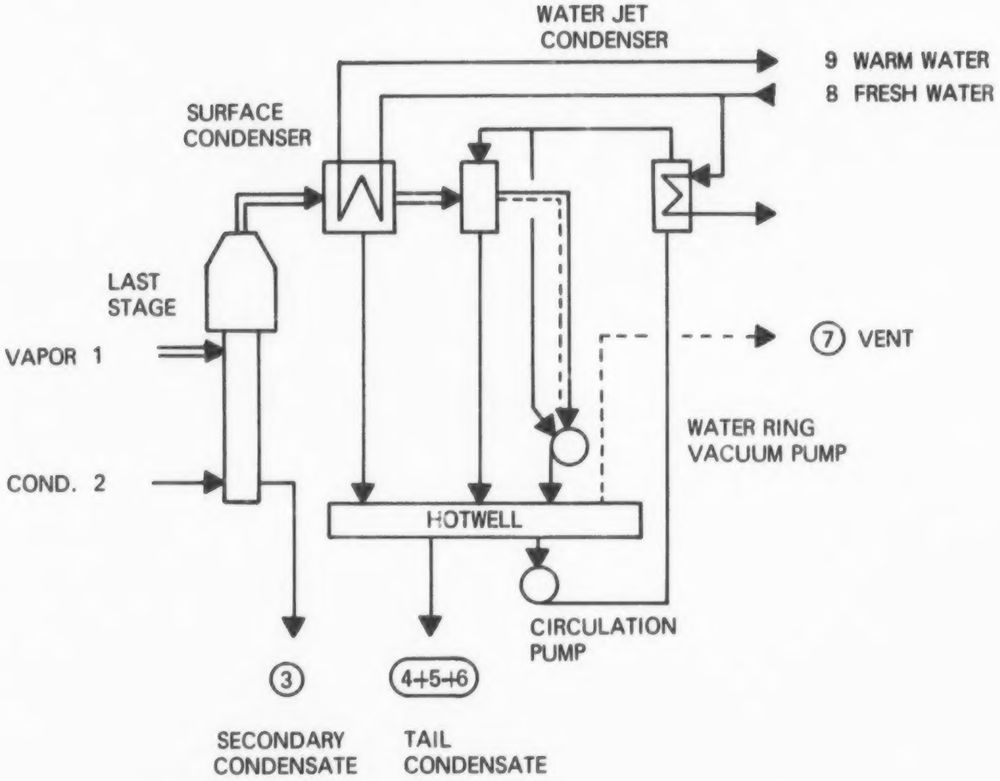
The quantity of combined evaporator condensates should be about 7.5 m^3 per metric ton of pulp (1800 gal/ton) without direct contact evaporation and with a dry solids yield of 1.5 kg per kg of pulp (1.5 tons/ton). The total evaporator condensates flow, however, is usually larger (see Table 5-3), because fresh water is added (see Figure 5-1). Surface condensers will reduce the amount of condensate (see Figure 3-4). To eliminate the addition completely, a heat exchanger can be installed and the hotwell condensate circulated through it for cooling and reuse in condenser and vacuum pulp (Figure 5-2). By feeding white liquor into the loop there will be a simultaneous gas scrubbing and condensate return to the white liquor system (section 3.2.1.2).


WATER JET CONDENSER
BAROMETIC SURFACE CONDENSER
9 WARM WATER
8 FRESH WATER
LAST STAGE
VAPOR 1
COND. 2
⑦ VENT
WATER RING VACUUM PUMP
HOTWELL
③
4+5+6
SECONDARY CONDENSATE
TAIL CONDENSATE

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 5-1

EVAPORATION PLANT SURFACE CONDENSER WITH WATER JET CONDENSER AND WATER RING PUMP


WATER JET CONDENSER
9 WARM WATER
8 FRESH WATER
SURFACE CONDENSER
LAST STAGE
VAPOR 1
COND. 2
⑦ VENT
WATER RING VACUUM PUMP
HOTWELL
CIRCULATION PUMP
③
4+5+6
SECONDARY CONDENSATE
TAIL CONDENSATE

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 5-2

EVAPORATION PLANT SURFACE CONDENSER WITH RECIRCULATED WATER JET CONDENSER AND WATER RING PUMP

5.3.2 Evaporator Condensate Segregation

A natural and very effective way of facilitating contaminated condensate treatment is to separate the condensates at their point of origin and group them according to their sulfur and BOD content. This procedure applies especially well to the evaporation plant, where most of the sulfur tends to concentrate in the tail end, and most of the BOD after the weak liquor feed.

The use of segregation is illustrated on an evaporation plant with 5 stages such as that presented in Figure 3-2. The liquor flow is 3-4-5-2-1 and stages 4 and 5, following the liquor feed stage, are equipped with two-stage venting through liquor preheaters (section 3.2.1.1). About 15 percent of the vapor to the stage condenses in the preheater. The evaporation plant condenser is divided into two surface condenser stages. About 13 percent of the vapor is condensed in the second stage and 2 percent in a water-ring vacuum pump that has indirect cooling. Under these circumstances the distribution of flows, sulfur, CH_3OH, and BOD will be approximately as presented in Table 5-4.

TABLE 5-4
CALCULATED EVAPORATOR CONDENSATE FLOW, SULFUR, METHANOL, AND BOD DISTRIBUTION FOR LIQUOR SEQUENCE 3-4-5-2-1 (4, 5, 6, 7)

Point of Release (No. refers to flows in Fig. 3-2)	Temp. °C (°F)	Flow(a) %	Sulfur(b) %	CH_3OH(c) %	BOD(d) %
2–Effect, condensate	115 (239)	21.0	1	1	1
2–Effect, vent					
3–Effect, condensate	100 (212)	18.0	1	2	2
3–Effect, vent					
4–Effect, condensate	85 (185)	15.3	3	24	22
4–Effect, preheater	80 (176)	2.7	3	33	32
4–Effect, vent				8(e)	8(e)
5–Effect, condensate	70 (158)	17.0	2	6	6
5–Effect, preheater	65 (149)	3.0	2	12	11
5–Effect, vent				4(e)	4(e)
6–Primary condenser	55 (131)	19.6	12	3	4
7–Secondary condenser	40 (104)	2.9	49	12	14
8–Vacuum pump	30 (86)	0.5	27	7	8
Total			100	100	100

(a) 100% flow = 6-7.5 m^3/t of pulp (1440-1800 gal/ton of pulp).

(b) 100% sulfur = 1-2 kg/t of pulp (2-4 lb/ton of pulp).

(c) 100% CH_3OH = 6-9 kg/t of pulp (12-18 lb/ton of pulp).

(d) 100% BOD = 7-10 kg/t of pulp (14-20 lb/ton of pulp).

(e) Already included in secondary condenser & vacuum pump.

By combining various effect condensates, for example, from effects 2 to 5, with those from the primary condenser, 90.9 percent of the condensates with 19 percent of the total reduced sulfur (TRS), and 35 percent of the total BOD at a mixing temperature of 86° C (187° F) are obtained without flashing. This flow may be reused within the process. The remaining 9.1 percent of the condensates will contain 81 percent of the sulfur and 65 percent of the BOD. This small flow can be rather easily treated, for instance by steam stripping. Then, by combining flows from 2, 3, and 5 with those of the primary condenser, 75.6 percent of the condensates are obtained that contain only 16 percent of the total sulfur and 13 percent of the total BOD. Other liquor sequences, vaporization distributions, and preheater locations will change the distribution of contaminants.

Condensate segregation requires special piping arrangements and usually causes a small increase in the primary steam consumption in the evaporation plant because of incomplete secondary condensate flashing.

Segregation of the hotwell condensates is needed solely for odor abatement. Hotwell condensates include those from the primary condenser, the secondary condenser, and the vacuum pump. These condensates alone contain 88 percent of the TRS in 23 percent of the condensate volume.

5.3.3 Weak Black Liquor Oxidation

An effective way to eliminate odors is to oxidize the weak black liquor.

By oxidizing the weak black liquor, the sulfide is converted to thiosulfate and the CH_3SH to CH_3SSCH_3. Therefore, H_2S and CH_3SH are not liberated in the evaporation process. Consequently the condensates will require little, if any, treatment for odor abatement. The oxidation can be quite effective, and different systems using air have been developed. One example is the British Columbia Research Council (BCRC) system that works as a weak black liquor and odorous gas oxidation system. This particular system uses bleach plant effluent containing rest chlorine as one gas scrubbing and oxidation agent, and so obviously it a bleach plant must be present.

There are, however, some drawbacks to weak liquor oxidation. During evaporation and storage the elemental sulfur generated tends to reconvert to H_2S, and the CH_3SSCH_3 to CH_3SH. Such reconversions will nullify to some extent the previous oxidation effort (8).

Another difficulty, especially with resinous softwoods, is the foaming of the weak liquor in the oxidation process. Its foaming tendency is a function of its concentration. At high concentrations the foaming decreases. Black liquors that can be oxidized as thick liquors may be impossible to oxidize as weak liquor, even up to 23 percent dry solids (8).

Furthermore, black liquor oxidation, weak or thick, will decrease the heat value of the dry solids by an average of 523 MJ per metric ton of pulp (0.45 × 10^6 BTU short ton of pulp). Also, the oxidizing air strips off odorous compounds from the liquor. Current trends are toward oxidation of thick black liquor just before its evaporation by direct contact with the recovery boiler flue gases. For more information on weak black liquor oxidation, see section 9.1.

5.4 Condensate Chlorination

It is possible to deodorize condensates from digesters and evaporators by mixing elemental chlorine (Cl_2) in the condensates. Since the chlorine demand of reduced sulfur compounds is high (Table 5-5) this is an expensive method unless there is an inexpensive source of chlorine available. For instance, in some mills bleach plant effluent containing rest chlorine is mixed with odorous condensates, and the combined effluent has neither H_2S nor chlorine odor (10).

TABLE 5-5
CHLORINE DEMAND OF REDUCED SULFUR COMPOUNDS FOR OXIDATION TO SULFUR (9)

Compound	pH	Cl_2 Demand kg Cl_2/kg Compound	Redox Potential (+) Volts
H_2S	4	9.2	0.25
H_2S	8	5.6	0.26
CH_3SH	4	6.7	0.45
CH_3SH	8	5.1	0.61
CH_3SCH_3	4	2.2	0.44
CH_3SCH_3	8	2.4	0.62
CH_3SSCH_3	4	1.9	0.58
CH_3SSCH_3	8	2.2	0.70

5.5 Condensate Stripping

Stripping the contaminated condensates has proved an efficient and economical way of removing odor and BOD. Condensate stripping is becoming the dominant treatment method. The two principal ways are air stripping and steam stripping. To facilitate stripping, certain preconditioning techniques should be utilized.

5.5.1 Condensate preconditioning

After the volume of condensates to be stripped has been reduced to the minimum feasible through using reduced fresh water input and condensate segregation, there are other conditions to be met.

A higher temperature of the released contaminated condensate will aid treatment by stripping. Air stripping will be more effective since the volatiles will have a higher vapor pressure. Similarly, steam stripping will require less steam for heating the condensates to the boiling point.

The condensates should have as low a pH as possible. A low pH means a high volatility for the ionized sulfur compounds, H_2S and CH_3SH (Figures 2-4 and 2-5); whereas, high pH (greater than 9) results in low volatility as well as foaming. High pH is the result of black liquor entrainment and, thus, may indicate insufficient drop and mist separation in the vapor flows or equipment overloading. The points to watch for high pH values are the blow tank and the evaporator drop separators.

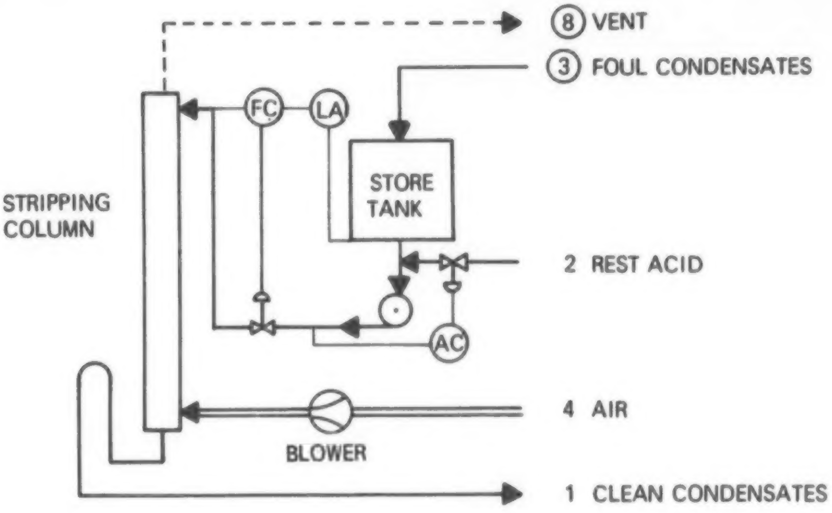
5.5.2 Air Stripping

A very simple condensate treatment is to strip the condensates in a multistage column (that is, a column with multiple trays) with a large countercurrent flow of air or flue air (Figure 5-3) (11).

Use of an atmospheric vent (see flow 5 in Figure 5-3) for air or flue gas stripping simply translates a water pollution problem into an air pollution problem. Although part of the TRS will be oxidized while feed and air or flue gas mix in the column, most of the TRS will pass out through the vent. With small feeds and air flows the vent can be connected to a boiler furnace or to an incinerator, but for air flows equal to thousands of cubic meters per hour this is hardly feasible.

Experience with working units (7) indicates that column features and performance are approximately as follows:

1. Tray type, bubble cap;
2. Liquid feed rate, F_{feed} m^3/h (F_{feed} gpm)
3. Tray number, 10-20;


⑧ VENT
③ FOUL CONDENSATES
FC
LA
STRIPPING COLUMN
STORE TANK
2 REST ACID
AC
4 AIR
BLOWER
1 CLEAN CONDENSATES

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 5-3

CONTAMINATED CONDENSATES AIR STRIPPING PLANT FLOW SHEET

4. Tray distance, 500 mm (20 in)
5. Column diameter, 130$\sqrt{F_{feed}}$ mm (2.44$\sqrt{F_{feed}}$ in)
6. Air flow, 18 × F_{feed};
7. Feed temperature, 65-70° C (149-158° F);
8. Feed pH, below 9;
9. TRS of feed, 130-320 g/m^3
10. BOD (CH_3OH) of feed, 390-1030 g/m^3
11. TRS removal, 80 percent; and
12. BOD removal, 0-10 percent.

Tripling the air flow will increase TRS removal to 84-94 percent and BOD removal to 10-15 percent.

The condensate feed must be as hot as possible and the pH must stay below 9. If pH rises above 9, reduced stripping efficiency and serious foaming problems will follow. The temperature of the ambient air will affect the feed temperature, but this effect is small, about 6° C (11° F).

If the pH of the condensates cannot be brought below 9, rest acid must be added to the condensate feed (see flow 2 in Figure 5-3). Rest acid is obtained, for example, from the manufacture of bleach plant ClO_2, and added at the feed pump suction. A control loop from after the pump can be set to keep the feed pH at a suitable level of about 7-8. Air or flue gas stripping will not remove more than 95 percent of TRS nor more than 15 percent of BOD at reasonable gas flow rates.

5.5.3 Steam Stripping

Steam stripping was first used about 25 years ago at Skoghall, Sweden (9). This steam stripping plant is still working and has been modernized. Steam stripping research was carried out in pilot plants (7, 12) and, subsequently, put into full-scale operation in a number of kraft mills.

5.5.3.1 Separate Steam Stripping Plants

Steam stripping seems to be the most feasible method of purifying contaminated kraft mill condensates. Steam stripping can be divided into two categories: TRS removal and BOD removal. Characteristic features of stripping TRS are strong pH dependency and low steam consumption, which is about 2 percent of the condensate feed for a 90 percent TRS removal. Characteristic features of stripping BOD are much lower pH dependency and high steam consumption, which is about 20 percent of the feed for a 90 percent BOD removal.

A typical steam stripping plant is shown in Figure 5-4. Condensates (flow 3) will enter a storage tank with level alarms. Rest acid addition (flow 2) is controlled to keep pH at 7-8 after leaving the tank to enter the preheater/primary condenser. Condensates then receive heat from outgoing stripped condensates in a heat exchanger. Then they pass a direct contact steam injector with temperature control to insure that column feed temperature is sufficient and constant. Condensates next pass down the column countercurrently to fresh steam injected at the bottom of the column. Condensate feed is kept constant by flow control subject to alarm from the storage tank-level monitor. Stripping steam flow also is kept constant, but the flow control set point will follow feed flow in a fixed ratio that can be adjusted. This ratio will essentially be equal to the steam/condensate ratio, taking into account steam consumed for heating the condensates to the boiling point.

The vapors rise through a fortifier section of the column countercurrently to condensate feedback and enter the primary condenser/preheater, where most of the vapor condenses.

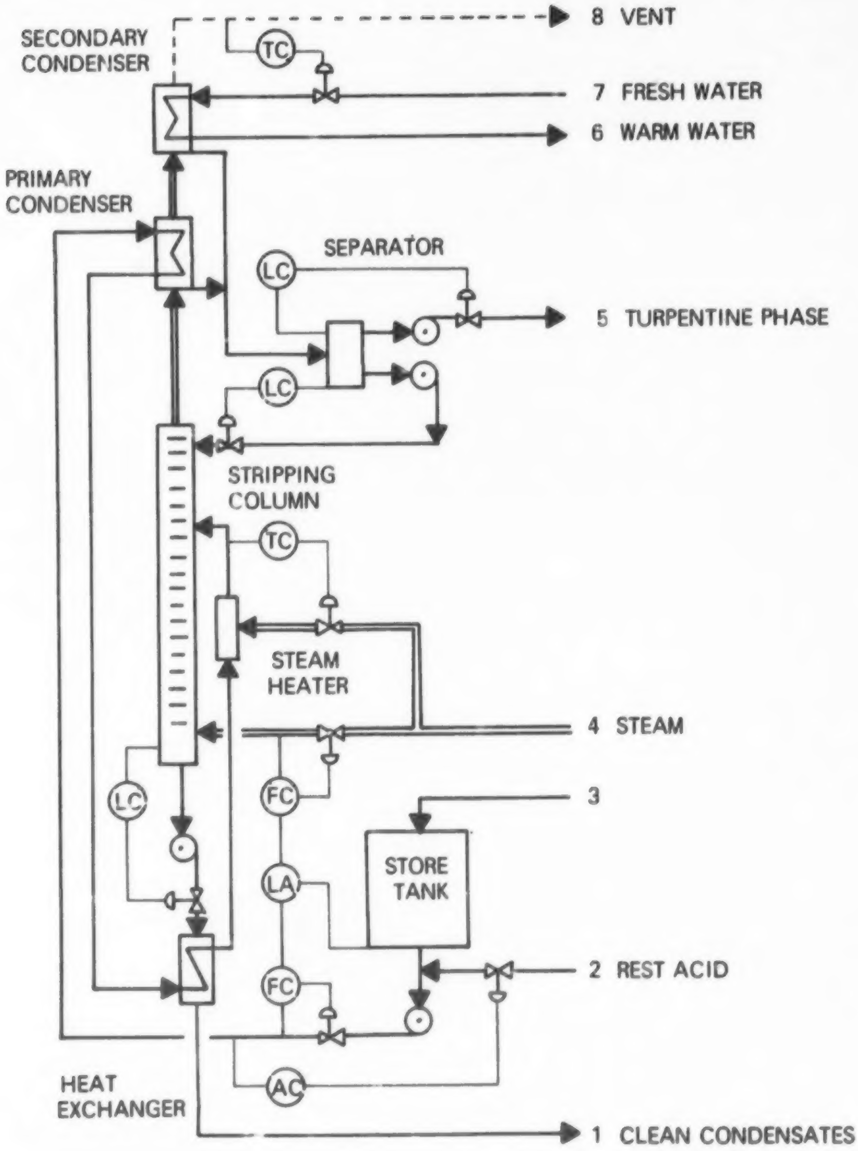

8 VENT
SECONDARY CONDENSER
TC
7 FRESH WATER
6 WARM WATER
PRIMARY CONDENSER
SEPARATOR
LC
5 TURPENTINE PHASE
LC
STRIPPING COLUMN
TC
STEAM HEATER
4 STEAM
LC
FC
3
STORE TANK
LA
2 REST ACID
FC
AC
HEAT EXCHANGER
1 CLEAN CONDENSATES

FIGURE 5-4

CONTAMINATED CONDENSATES STEAM STRIPPING PLANT FLOW SHEET

The noncondensables and the rest of the water vapor pass to the secondary condenser, which serves as a final condenser and gas cooler. The cooling is controlled by the outgoing gas temperature, which will stay constant. Adjusting the set point of the controller means adjusting the temperature and the dew point of the noncondensable gases from the vent (flow 8 in Figure 5-4). By adjusting the dew point, these gases can be kept at a humidity level (40%) that will greatly diminish the explosion risk.

The column condensates flow to a separator where eventually turpentine and other organic compounds may form an oily layer to be drawn off with a level control and piped to incineration (flow 5 in Figure 5-4). The underflow is pumped back to the column fortifier section top under level control. To give a very general idea of how to dimension and what to expect from a steam stripping column, the following data are given:

1. Tray type, bubble cap:
2. Steam flow rate, F_{steam} in metric tons per hour (F_{steam} short ton/hour)
3. Tray number, 10-20;
4. Tray distance, 500 mm (20 in);
5. Column diameter, $780\sqrt{F_{steam}}$ mm ($29.2\sqrt{F_{steam}}$ in)
6. Feed pH, below 9;
7. TRS of feed, 210 g/m^3
8. BOD of feed, 300 g/m^3

The removal percentage as a function of the steam/condensate ratio is approximately as shown in Figure 5-5. A lower pH of the feed would improve these removal rates for H_2S, especially at low steam/condensate ratios. After the contaminants have been stripped out of the condensate, and the main part of the water vapor condensed, the remaining gases are usually incinerated. Such gases may be incinerated in either the lime kiln, a separate incinerator, or possibly the recovery boiler.

5.5.3.2 Evaporation Steam Stripping Plants

Stripping of the condensates is usually performed in a separate stripping column with fresh steam. One way to reduce the high treatment costs involved is to combine this stripping with the evaporation plant, using "secondary steam" from the black liquor evaporation step. Such an arrangement is shown in Figure 5-6.

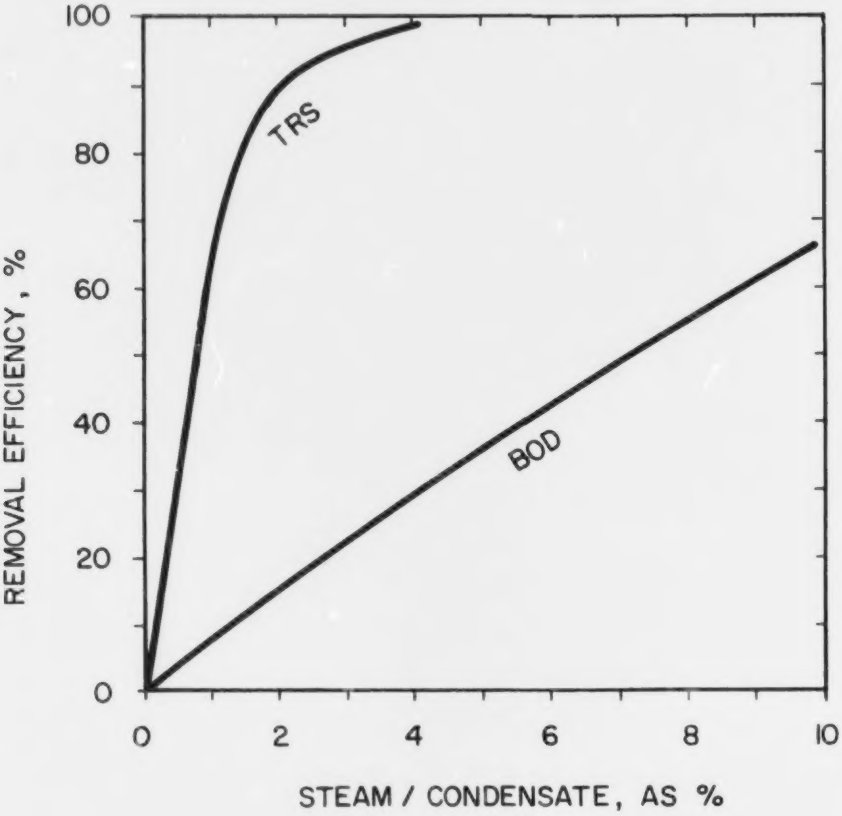


FIGURE 5-5

STRIPPING EFFICIENCY FOR DIFFERENT STEAM-CONDENSATE RATIOS WITH 10 THEORETICAL PLATES

The stripping column is placed on top of the second effect, similarly to the alcohol stripping in a sulfite spent liquor evaporation plant. All dirty condensates are piped to the stripping column, where the stripping efficiency is 95 percent. The CH_3OH stripped off is withdrawn through the liquor preheater of the third effect together with a small amount of steam and is condensed to form an 8-10 percent CH_3OH water solution. The CH_3OH is recovered in a small stripping column and destroyed by burning. Alternatively, it can be recovered and sold. The total BOD-removal of the condensates by this stripping arrangement is estimated at 90 percent. If the stripping column is placed on top of the second evaporator effect, the heating surface of the evaporation plant has to be increased by approximately 7 to 8 percent. This increase is necessary to compensate for the pressure loss in the column and the lower condensation temperature in the third effect. The steam consumption of the evaporation plant increases by 5 to 7 percent.

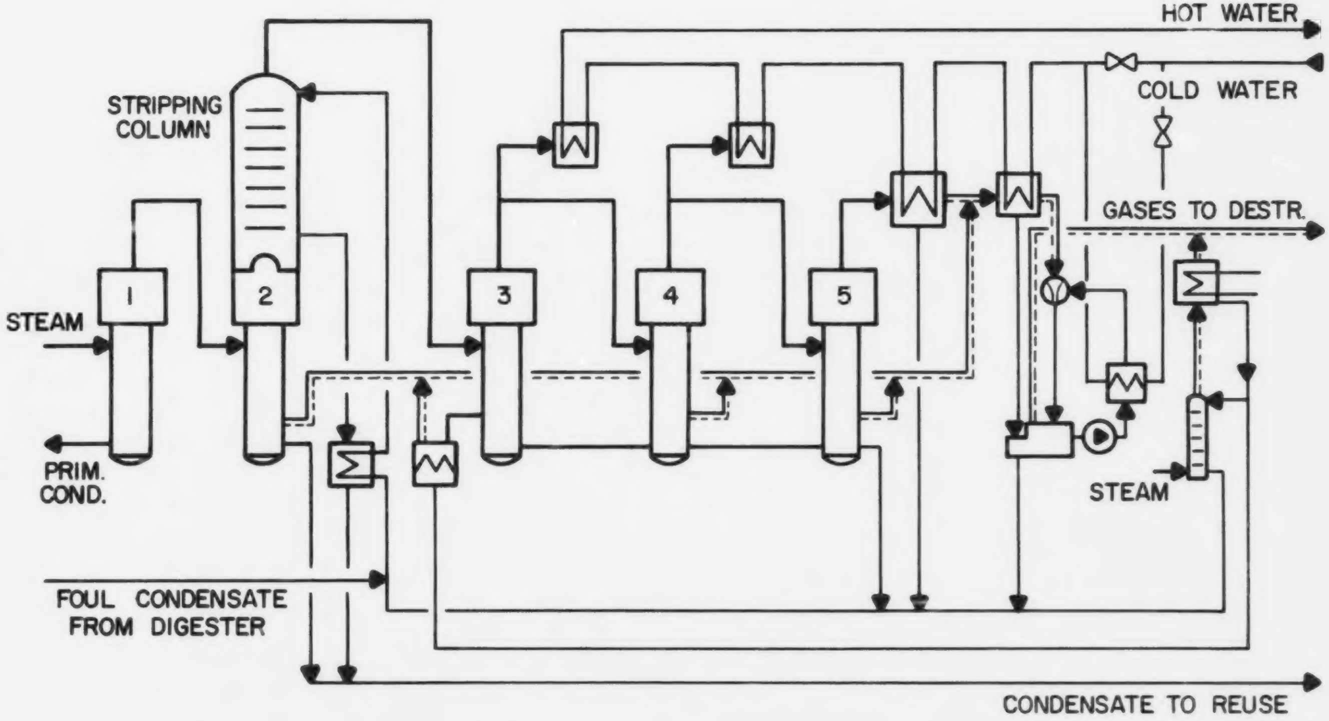

HOT WATER
COLD WATER
GASES TO DESTR.
STRIPPING COLUMN
STEAM
PRIM. COND.
1
2
3
4
5
STEAM
FOUL CONDENSATE FROM DIGESTER
CONDENSATE TO REUSE

FIGURE 5-6

CONDENSATE STRIPPING IN AN EVAPORATION PLANT (13)

By using the stripping arrangement shown in Figure 5-6, the evaporation plant will produce thick liquor and clean, practically distilled water for reuse, plus concentrated volatile organics as a byproduct.

5.5.4 Condensate Finishing

Condensate finishing may be feasible when very high removal efficiencies of greater than 99 percent are required. Instead of stripping with an excessively large steam/condensate ratio, enough stripping steam is first used to decrease TRS by 90 or 95 percent, and then the stripped condensate is treated with ozone, chlorine, or activated carbon (14). Condensate stripped of TRS may be finished in a biological treatment plant where most of the remaining traces of TRS and BOD are removed. Biological condensate finishing can be accomplished if the mill already has a biological treatment plant for its other wastewaters.

5.5.5 Condensate Reuse

Condensate reuse includes reuse of both treated and untreated condensates. When using treated condensates that have been stripped of their TRS and BOD, there are no reuse problems since the treated condensate is clean, hot, distilled water.

When reusing condensates that have been stripped of their TRS components only, the BOD components will come out from the process at some other point. If the components are recirculated, they will build up within the process unit until such a level is reached that discharge takes place. The best way to treat such condensates is to direct the discharge of BOD components into the recovery boiler through the black liquor.

When using untreated contaminated condensates, the TRS must be removed since it will either go down the drain to the receiving waters or it will start circulating and building up until it is discharged to the atmosphere and/or to the water. A possible solution is to put the TRS back into the white liquor, where it will provide part of the sulfide and decrease the sulfur make-up demand.

5.5.5.1 Pulp Washing

Untreated contaminated condensates have been used for pulp washing, especially in mills with direct blow heat recovery (see section 5.2.1). But such an arrangement causes air pollution from washer hoods, and water pollution from the pulp screening, if an open-screening system is used. A closed-screening system will reintroduce the water pollutants, raise their level, and increase air pollution.

Before contaminated condensates are used for pulp washing, they should be stripped completely for open-screening systems, and at least of their TRS components for closed-screening systems. A stripped condensate is a very good washing liquid, namely hot distilled water. The total condensate amount, without adding fresh water, will be about 7.5-8.5 m^3/per metric ton of pulp (1800-2000 gal/ton). The amount will depend upon whether there is continuous or batch digestion. Of this amount, about 8 m^3 per metric ton of pulp (1900 gal/ton) can be used for washing pulp, thus meeting the whole wash water demand.

5.5.5.2 Lime Kiln Flue Gas Scrubbing

Using contaminated condensates as scrubbing liquids in lime kiln flue gas scrubbers amounts to stripping them with hot gases while they reciprocally wash particulates from the gases. The result is increased air pollution caused by TRS. To use stripped condensates in lime kiln or flue gas scrubbers offers no advantage, since ordinary fresh water will do the same job while additionally picking up heat from the hot gases. Stripped condensates are hot distilled water and should be used in proper applications, such as washing pulp in the washing department or in the bleach plant. Fresh water demand for a lime kiln scrubber is about 4 m^3 per metric ton of pulp (960 gal/ton).

5.5.5.3 White Liquor Liquid Makeup

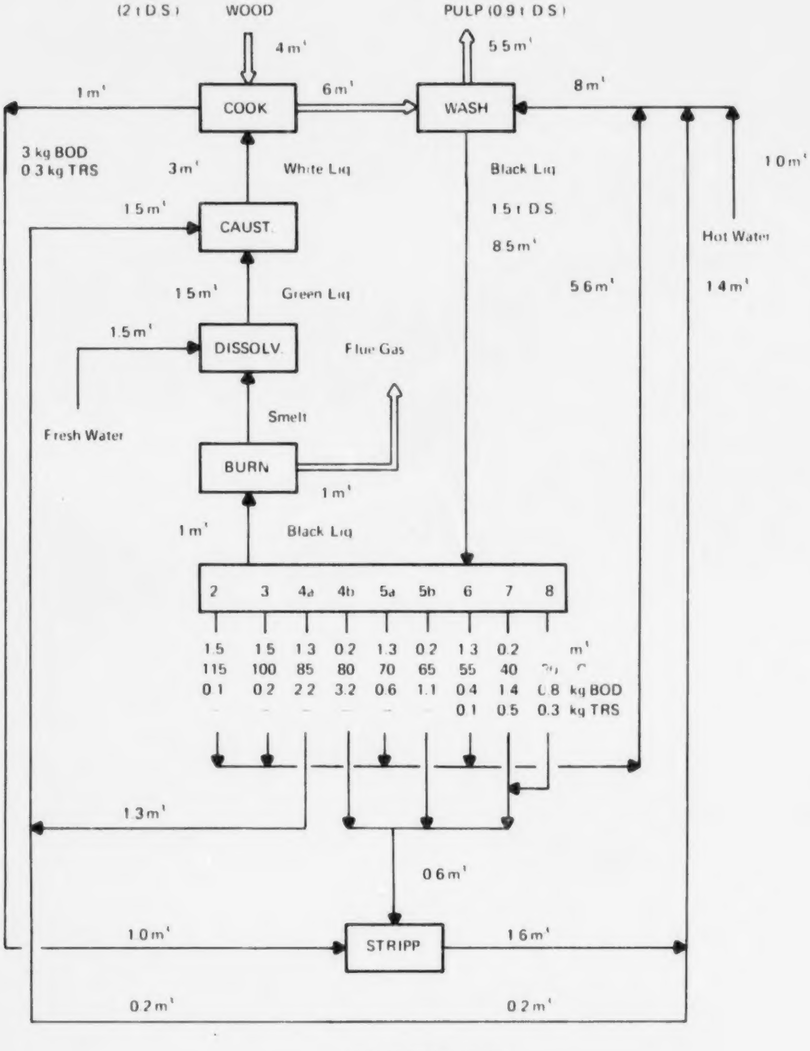
In the digester, the liquid/dry wood ratio can be trimmed by black liquor recirculation. The necessary liquid makeup to the white liquor can be supplied at three points, namely in the smelt dissolving tank, in the mud washers, and in the white liquor itself.

The smelt dissolving tank requires liquid at about a rate of 1.5 m^3 per metric ton of pulp (360 gal/ton). The liquid should preferably be cool water, since the heat input to the smelt dissolver is already so great that addition of hot water would cause vaporization of both water and volatile and odorous substances. Condensates, therefore, are not suitable for smelt dissolver liquor makeup unless they are first stripped of TRS and cooled.

The mud washers need hot water and usually 50 percent of the white liquor liquid demand, approximately 1.5 m^3 per metric ton of pulp (360 gal/ton), enters the process this way. Contaminated condensates will cause odor problems at the mud washer, but TRS stripped condensates may be used although BOD components then will be fed back into the process.

If the mud washer system is highly effective, that is, if it will work with less wash water than the 1.5 m^3 per metric ton of pulp (360 gal/ton), the remaining makeup liquid can be supplied directly to the white liquor. Treated or untreated condensates can be used since odorous compounds will, for the most part, be absorbed by the alkali of the white liquor. The BOD level will rise, of course.

A plan for condensate segregation, stripping, and reuse is suggested in Figure 5-7. This plan will require about 1.5 m^3 per metric ton of pulp (360 gal/ton) of fresh water makeup and about 1 m^3 per metric ton of pulp (240 gal/ton) of hot water makeup for the pulping cycle. Seven percent of the combined digester and evaporator condensates, containing 91 percent of the combined TRS and 73 percent of the combined BOD, are stripped and used for washing pulp and lime mud. Seventeen percent of the BOD is returned to the white liquor. Ten percent of the BOD and 9 percent of the TRS are returned to pulp washing. Approximately 50 percent of these contaminants will remain with the pulp and get washed out during screening; the rest will return to the black liquor.



(2 t D S)
WOOD
4 m^3
PULP (0 9 t D S)
5 5 m^3
1 m^3
COOK
6 m^3
WASH
8 m^3
3 kg BOD
0 3 kg TRS
3 m^3
White Liq
Black Liq
1 0 m^3
1.5 m^3
CAUST.
1 5 t D S.
8 5 m^3
Hot Water
1 5 m^3
Green Liq
5 6 m^3
1 4 m^3
1.5 m^3
DISSOLV.
Flue Gas
Smelt
Fresh Water
BURN
1 m^3
1 m^3
Black Liq
2 3 4a 4b 5a 5b 6 7 8
1.5 1 5 1 3 0 2 1.3 0 2 1 3 0.2 m^3
115 100 85 80 70 65 55 40 30 °C
0 1 0 2 2 2 3.2 0.6 1.1 0 4 1 4 0.8 kg BOD
– – – – – – 0 1 0.5 0.3 kg TRS
1.3 m^3
0 6 m^3
1 0 m^3
STRIPP
1 6 m^3
0.2 m^3
0 2 m^3

FIGURE 5-7

SIMPLIFIED LIQUID FLOW SHEET FOR KRAFT PROCESS WITH CONDENSATE SEGREGATION, STRIPPING, & REUSE

5.6 References

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CHAPTER 6

BROWN STOCK WASHER GASES

After mixing with the original liquor and added black liquor, the pulp passes from the blow tank to the washing plant. The washing process is a minor source of air pollution compared to combustion, evaporation, and digestion. Generally, the washing produces large quantities of ventilation air slightly contaminated with organic sulfur compounds through contact with the black liquor. The amount of air and of sulfur compounds will mainly depend on the type of washing process and equipment and to a minor degree on wood, sulfidity, pH, temperature, and other factors that are generally determined by the production process. The two main washing processes are displacement washing and diffusion washing.

6.1 Displacement Washing

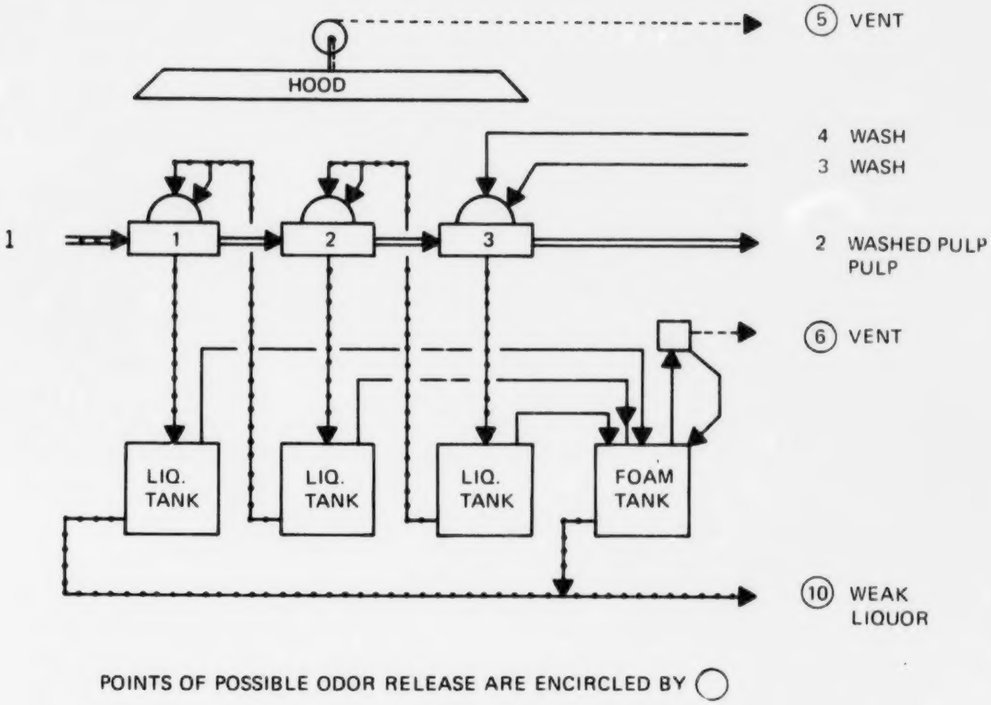
Displacement washing usually takes place on rotary drum filters using air for maintaining the pressure difference over the washed pulp sheet. Thus, the hot black liquor is exposed to large quantities of air. This exposure will have two effects. One effect, for example, is that a portion of the reduced sulfur in the black liquor will be oxidized and will decrease the subsequent odor generating capacity of the black liquor during evaporation. The other effect is that part of the reduced sulfur will become volatile and will contaminate the air.

6.1.1 Vacuum Washers

The most common type of kraft pulp washer is the vacuum washer (Figure 6-1). The two main points of odor release to the atmosphere are the hood vent (flow 5 in Figure 6-1), with large flows of slightly contaminated air and the foam tank vent (flow 6 in Figure 6-1), with smaller flows of more polluted air. Tables 1-2, 1-3, and 1-4 summarize typical emissions from these sources.

Because of their large volume and low concentration of odorous components, the only practical way of treating washer gases, especially those from the hood vent, is to incinerate them in an existing boiler. For example, the gases from the washer vents are used as part of the combustion air in an auxiliary furnace or a black liquor recovery boiler at several U.S. and Swedish mills. Proper safety precautions must be designed into the system. These precautions include condensate traps, rupture disks, flame arresters and flame control, and emergency vents. The smaller flow rate of the foam tank vent gases allows incineration in the lime kiln. The sulfur content of foam tank gases varies with their source, that is, whether softwood or hardwood, see Table 6-1.

Some mills use contaminated condensates from blow heat recovery accumulators or evaporators for washing. This practice will increase the odor release from the washers significantly. The hood vent TRS emission may increase 5 to 15 times, and the foam tank vent TRS emission may increase from 20 percent to 4.5 times when changing from fresh hot water wash to condensate wash (1). The abatement method is to strip the condensates before use.



⑤ VENT
HOOD
4 WASH
3 WASH
1
1
2
3
2 WASHED PULP PULP
⑥ VENT
LIQ. TANK
LIQ. TANK
LIQ. TANK
FOAM TANK
⑩ WEAK LIQUOR
POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 6-1
VACUUM WASHERS FLOW SHEET

6.1.2 Pressure Washers

Pressure washers have closed hoods with blowers circulating air for maintaining the pressure difference across the pulp sheet (Figure 6-2). The hood vent (flow 5 in Figure 6-2) and the foam tank vent (flow 6 in Figure 6-2) will both have a small flow rate and a high sulfur concentration compared to the vacuum washer hood vent. Black liquor oxidation and release of reduced sulfur to the atmosphere will be less, too.

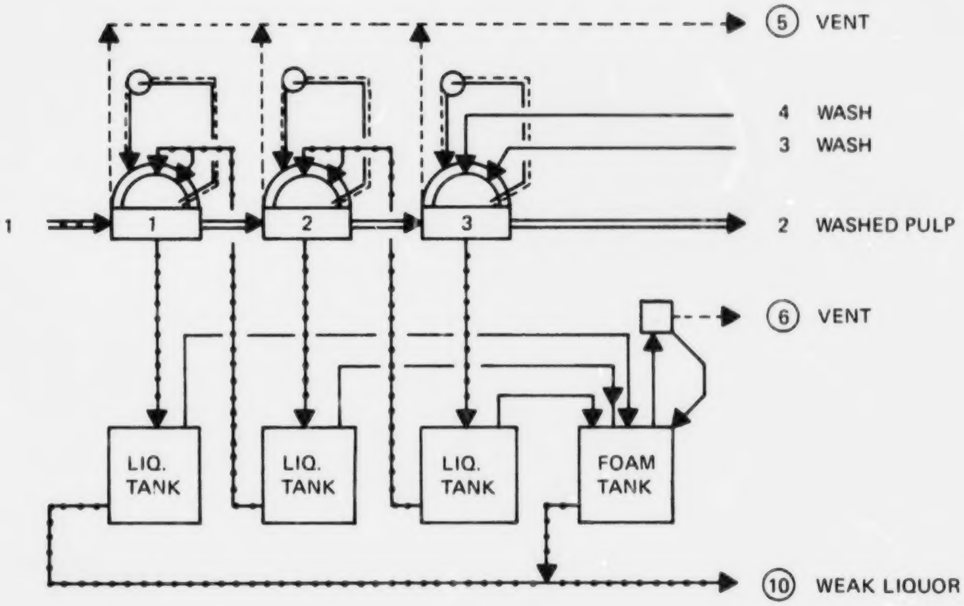
Odor abatement is much easier than for a vacuum washing plant and can best be accomplished by incineration of the vent gases in the lime kiln.

6.2 Diffusion Washers

Diffusion washing usually takes place in a closed reactor, and ideally there is no air involved. Therefore, black liquor oxidation and odor release are very small, when compared with displacement washers.

TABLE 6-1
FLOWS, COMPOSITION AND SULFUR RELEASE OF VACUUM WASHER FOAM TANK VENT GASES (2)

Wood Species	Flow m³/t (ft³/ton)	Component	Sulfur kg/t	Sulfur (lb/ton)
Pine	64	H_2S	0	0
	(1930)	CH_3SH	0.03	0.06
		CH_3SCH_3	0.06	0.12
		CH_3SSCH_3	0.04	0.08
		Total	0.13	0.26
Birch	65	H_2S	0	0
	(2080)	CH_3SH	0.02	0.04
		CH_3SCH_3	0.13	0.26
		CH_3SSCH_3	0.13	0.26
		Total	0.28	0.56

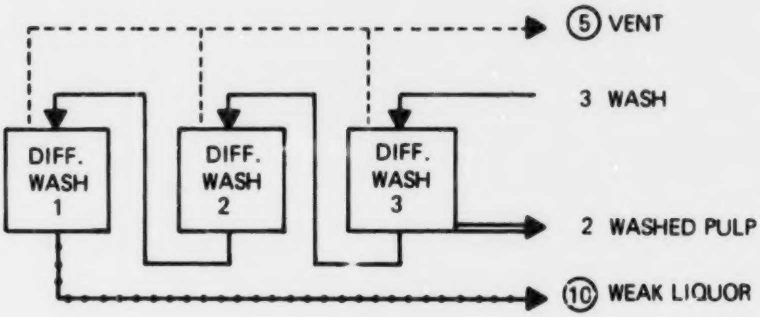

⑤ VENT
4 WASH
3 WASH
1
1
2
3
2 WASHED PULP
⑥ VENT
LIQ. TANK
LIQ. TANK
LIQ. TANK
FOAM TANK
⑩ WEAK LIQUOR

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 6-2
PRESSURES WASHERS FLOW SHEET

6.2.1 Batch Diffusers

Batch diffusers can still be found in old mills, but in many cases have been replaced by vacuum washers (Figure 6-3). Because of the batch operation there is liquor-air contact during blowing, washing, and emptying of the diffuser. Consequently, there is some black liquor oxidation and odor release, symbolized by flow 5 in Figure 6-3. The sulfur release will be difficult to determine and abate. Continuous venting to the lime kiln is probably the best method of gas treatment.



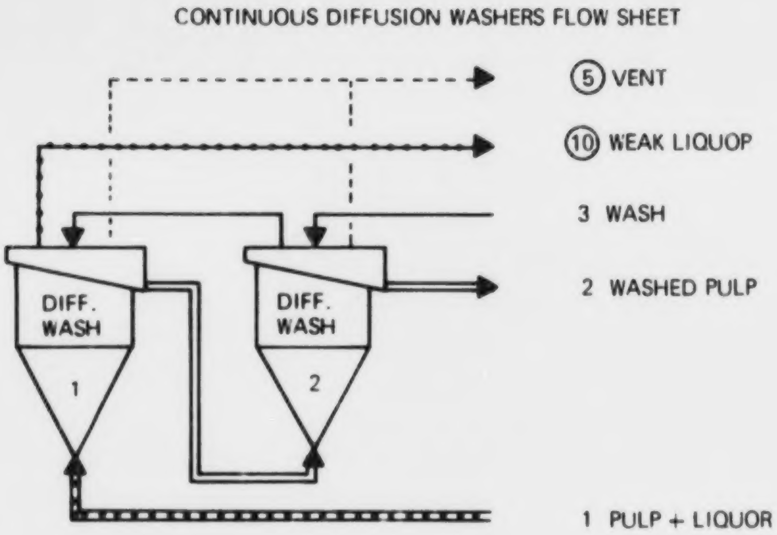
FICURE 6-3

BATCH DIFFUSION WASHERS FLOW SHEET

6.2.2 Continuous Diffusers

Continuous diffusers have been integrated with continuous digesters for the past decade. They are also now made as separate washers (Figure 6-4). The washing process is closed-off to minimize air infiltration. Thus, the oxidation of the black liquor and the subsequent release of reduced sulfur, symbolized by flow 5 in Figure 6-4, are kept at a minimum. The reduced sulfur is rather easily contained and is incinerated in the lime kiln.

Scrubbing of washer gases with an alkaline solution, such as white liquor, is not generally practiced since the washer gas TRS is predominantly nonionizable sulfur compounds.


CONTINUOUS DIFFUSION WASHERS FLOW SHEET
⑤ VENT
⑩ WEAK LIQUOP
3 WASH
2 WASHED PULP
DIFF. WASH
1
DIFF. WASH
2
1 PULP + LIQUOR

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 6-4
CONTINUOUS DIFFUSION WASHERS FLOW SHEET

6.3 References

1. *Atmospheric Emissions from the Pulp and Paper Manufacturing Industry.* EPA-450/1-73-002. September 1973. (Also published as NCASI Technical Bulletin No. 69, February 1974.)

2. Kekki, R., *Kraft Mill Odor Abatement by Condensate Stripping and Waste Gas Incineration.* M.S. Thesis, Wood Industry Department, Helsinki Technical University, Finland, September 18, 1969 (Finnish).

CHAPTER 7

STORAGE TANK VENT GASES

All storage tanks, especially black liquor tanks that hold sulfide-containing liquor, are potential air polluters when vented to the atmosphere. All of the storage tanks of a mill together, however, are a minor source of air pollution, even smaller than the vacuum washer hoods.

7.1 Storage Tank Vent Gas Composition

The liquor in the tank is usually hot, and the tank vent will emit water vapor contaminated mainly with organic reduced sulfur compounds. The composition of the noncondensable gases is rather similar to that of the washer gases. The main factors influencing release of odorous gases are liquor sulfide concentration, pH, and temperature. These factors are fixed by external circumstances (i.e., the general production process), and cannot be changed except within a very narrow range.

7.2 Storage Tank Vent Gas Treatment

The fact that storage tanks are dispersed over the mill, thus constituting several air pollution sources, makes their treatment quite difficult. An effective program is to connect all storage tank vents to a central duct leading to an incinerator or an oxidation tower. This system is applied in one Scandinavian mill (1) and at least one U.S. mill (2).

One way of reducing the release of odor from black liquor storage tank vents is to use weak black liquor oxidation. (See Chapter 9.)

7.3 References

1. *Air Pollution Abatement Problems of the Forest Industry*. Statens Naturvardsverk (Sweden). Publication 1969: 3, July 1969.

2. Michigan Department of Natural Resources, Division of Air Pollution Control. Staff Activity Report dated April 24, 1973.

CHAPTER 8

TALL OIL RECOVERY GASES

When pulping softwood with an alkaline process, recovery of tall oil can be quite profitable. Soap is skimmed from weak, intermediate, and strong black liquor storage tanks and evaporators, and from black liquor oxidation plants. To liberate the fatty acids from their sodium salts, the soap is acidified with sulfuric acid (H_2SO_4). The H_2SO_4 will also displace other weak acids present, such as H_2S and CH_3SH, creating a potential air pollution problem. The two factors with the greatest influence on the odor release are the soap washing efficiency and the recovery mode (batch or continuous). Tall oil recovery gases are minor odor sources in the kraft mill.

8.1 Batch Tall Oil Recovery

A typical batch tall oil plant flow scheme is depicted in Figure 8-1. The major odor emission point is the boiler vent (flow 5 in Figure 8-1). When H_2SO_4 is mixed with soap, the sulfide of the residual black liquor, which has not been washed away, reacts to form H_2S. Thus, there is first a sudden surge followed by a gradual decrease in evolution of H_2S. Another surge of H_2S may follow when the brine is neutralized with white liquor. The major part of the noncondensable flow is air. The H_2S concentration may vary between zero and 2 percent. Other TRS components and some typical concentrations are given in Table 8-1. Flow rates and sulfur emission rates of TRS are given in Table 8-2.

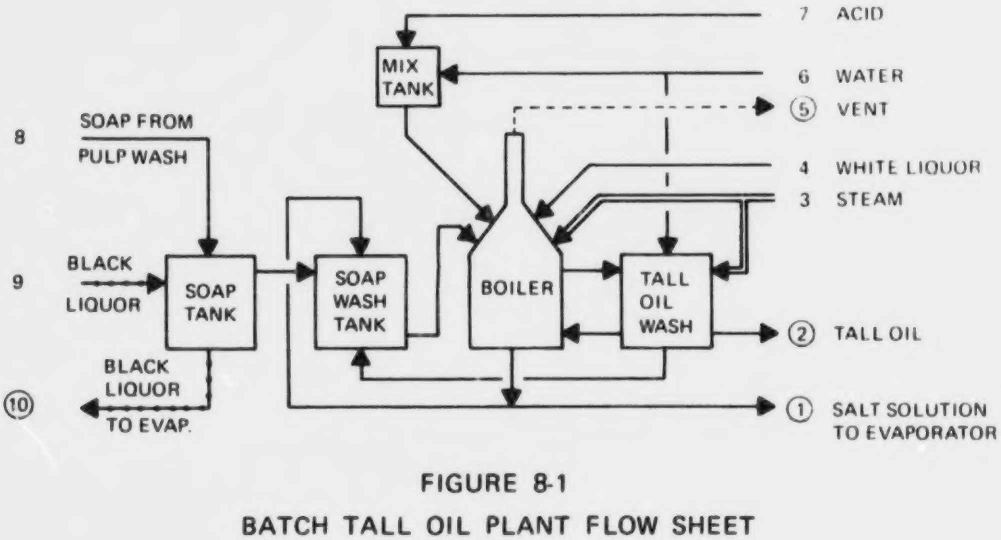

7 ACID
MIX TANK
6 WATER
⑤ VENT
8 SOAP FROM PULP WASH
4 WHITE LIQUOR
3 STEAM
9 BLACK LIQUOR
SOAP TANK
SOAP WASH TANK
BOILER
TALL OIL WASH
② TALL OIL
BLACK LIQUOR TO EVAP.
⑩
① SALT SOLUTION TO EVAPORATOR

FIGURE 8-1
BATCH TALL OIL PLANT FLOW SHEET

TABLE 8-1

BATCH TALL OIL RECOVERY PLANT TRS COMPONENTS AND TYPICAL CONCENTRATIONS (1, 2)

TRS Component	Typical Concentration g/m^3	(gr/cu ft)
H_2S	8.7	(3.8)
CH_3SH	0.3	(0.13)
CH_3SCH_3	0.2	(0.09)
CH_3SSCH_3	0.03	(0.01)

TABLE 8-2

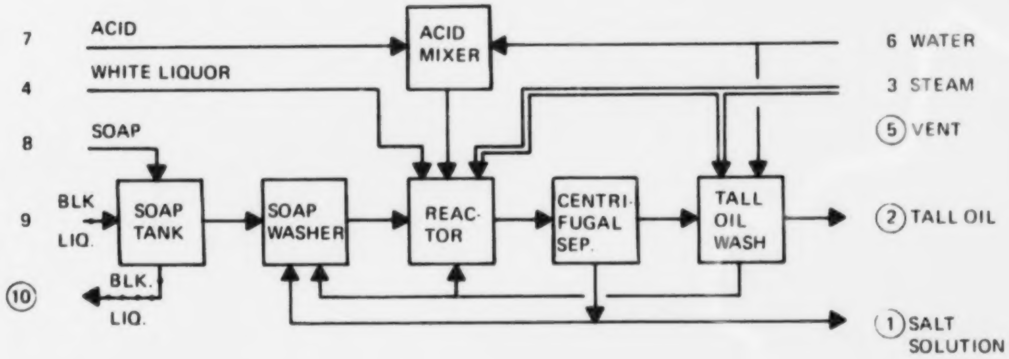
TALL OIL RECOVERY NONCONDENSABLE GAS FLOWS AND REDUCED SULFUR EMISSIONS (1) (2)

Condition	Gas Flow m^3/t	(cu ft/ton)	TRS Emission kg of S/t	(lbs/ton)
Maximum	20	(641)	0.66	(1.32)
Mean	11	(352)	0.15	(0.30)
Minimum	1	(32)	0.01	(0.02)

Since most of the TRS is H_2S, one treatment method often used is to duct the boiler vent (flow 5 in Figure 8-1) directly to a white liquor scrubber.

8.2 Continuous Tall Oil Recovery

A typical continuous tall oil plant flow scheme is depicted in Figure 8-2. The major odor emission point is the reactor vent (flow 5 in Figure 8-2). The flow is much smaller but more concentrated in TRS than for the batch process. There are no surges of H_2S, but a continuous flow. The best treatment method is to apply a white liquor scrubber to the vent.


7 ACID
4 WHITE LIQUOR
8 SOAP
9 BLK LIQ.
⑩ BLK. LIQ.
ACID MIXER
SOAP TANK
SOAP WASHER
REACTOR
CENTRIFUGAL SEP.
TALL OIL WASH
6 WATER
3 STEAM
⑤ VENT
② TALL OIL
① SALT SOLUTION

POINTS OF POSSIBLE ODOR RELEASE ARE ENCIRCLED BY ○

FIGURE 8-2
CONTINUOUS TALL OIL PLANT FLOW SHEET

8.3 References

1. *Air Pollution Abatement Problems of the Forest Industry*. Statens Naturvardsverk (Sweden). Publication 1969:3. July 1969.

2. EKONO Oy, Helsinki, Finland, files.

CHAPTER 9

BLACK LIQUOR OXIDATION

Black liquor oxidation is extensively applied to facilitate odor control and chemical recovery in kraft pulp mills. Its immediate purpose is oxidation of Na_2S to innocuous salts to prevent the release of H_2S. Black liquor oxidation can be performed on either weak or strong black liquor by air or molecular oxygen. Overall reviews of black liquor oxidation practices have been prepared by Collins (1), Landry (2), Hendrickson (3), and Blosser and Cooper (4).

9.1 Weak Black Liquor Oxidation – Air

Weak black liquor can be oxidized with air to decrease reduced sulfur emissions from both multiple-effect and direct-contact evaporation systems. Systems in extensive use for weak black liquor oxidation include sieve tray towers (5), porous carbon black diffusers (6), packed absorption towers (7), vertical-slat falling-film packed towers (8), and agitated air spargers (9). Rotating fluid contactors (10) and pressurized vessels (11) are used to a lesser extent for weak liquor oxidation.

A previous survey by Blosser and Cooper (4) indicates that it is possible to obtain consistently high efficiency of Na_2S oxidation with the porous diffuser (Collins) and the sieve tray tower (Trobeck), provided that sufficient gas-liquid interfacial contact areas and air flow rates are used and that liquor and Na_2S loadings are kept sufficiently low. Less effective performance is observed for packed towers because of inadequate liquor retention times and for agitated air spargers because of frequent mechanical breakdowns.

Most weak black liquor oxidation systems, employing air in the United States, are located in the Pacific Northwest, upper Midwest, and Northeast, where highly resinous pine wood species are not pulped. Blosser and Cooper (4) report the following problems with weak black liquor oxidation systems using air:

1. Excessive foaming when pulping highly resinous pine wood species,
2. Incomplete Na_2S oxidation efficiency caused by improper or under-design of systems,
3. System overload caused by increased pulping capacity without expansion of existing facilities, resulting in inadequate liquor retention time, and
4. Inability to achieve effective oxygen mass transfer from air into the black liquor.

9.1.1 Porous Plate Diffusers

Collins (12) reports on the development of a two-stage system for weak black liquor oxidation with air in consecutive aeration and deaeration steps (see Figure 9-1). The aeration stage employs passage of black liquor across a series of horizontal porous plates arranged vertically in a parallel flow arrangement. Air is blown consecutively in series through the porous plates in a crossflow configuration to create gas-liquid interfacial contact by the generation of foam. The liquor depth on the plates is normally 10 to 20 cm (4 to 8 in).

The air-foam-liquor mixture flows off the plates for deaeration in a retention tank to provide for gas-liquid phase separation. Foam is dissipated by mechanical foam breakers atop the deaeration tank, and liquid droplets entrained in the exit gas stream are returned to the deaeration tank via a cyclone separator, as shown in Figure 9-1. Recent studies by Van

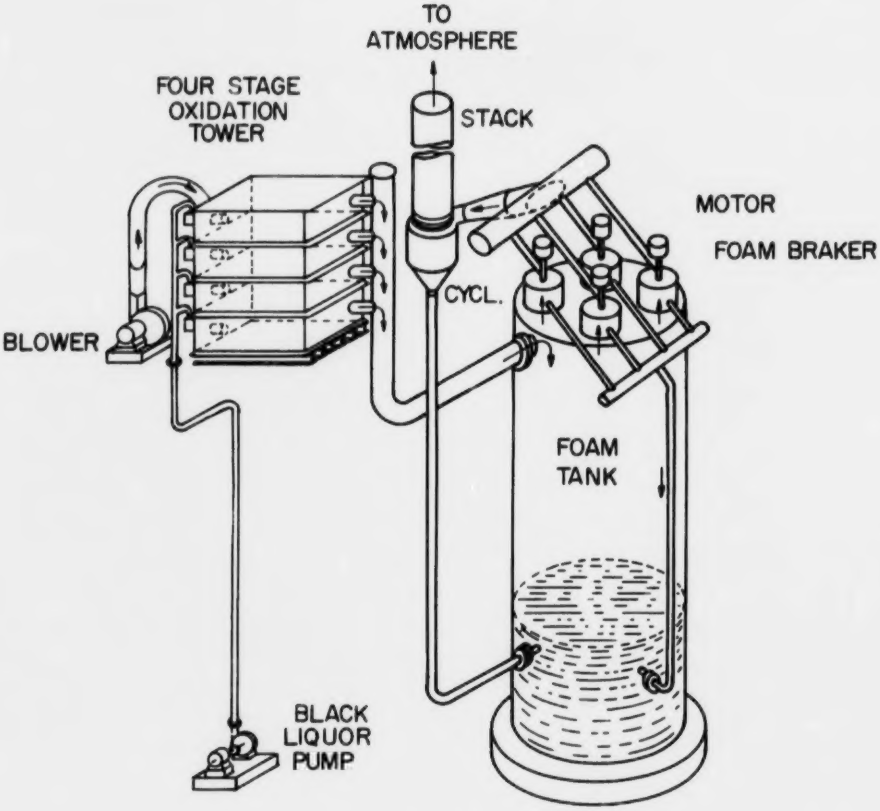


FIGURE 9-1
COLLINS POROUS PLATE DIFFUSER WEAK BLACK LIQUOR
OXIDATION SYSTEM (14)

Donkelaar (13) and Shah and Stephenson (14) indicate that the Na_2S concentration in weak black liquor can be reduced to below 100 mg/l by a porous plate diffuser oxidation system. Design and operating parameters calculated from published data for the two mills are presented in Table 9-1. The systems are not normally suitable for highly resinous pine black liquors because of excessive foaming.

TABLE 9-1
DESIGN AND OPERATING PARAMETERS FOR POROUS PLATE DIFFUSER BLACK LIQUOR OXIDATION SYSTEMS (13, 14)

Parameter	Mill A (13)	Mill B (14)
Production, t (ton)/day	450 (500)	180 (200)
Liquor flow, m^3/h (gpm)	205-227 (900-975)	68-108 (300-475)
Air flow, m^3/h (cfm)	25.600 (16,500)	13,700 (8,850)
Power, kW (hp)	186 (250)	75 (100)
Plate area, m^2 (ft^2)	650 (7,000)	312 (3.350)
Na_2S loading, $kg/m^2/h$ ($lb/ft^2/hr$)	2.4-2.9 (0.5-0.6)	1.2-2.4 (0.2-0.5)
Liquor loading, $m^3/m^2/h$ ($gal/ft^2/hr$)	0.30-0.35 (7.4-8.6)	0.22-0.35 (5.3-8.5)
Air loading, $m^3/m^2/h$ ($cu\ ft/ft^2/hr$)	39 (128)	44 (144)
Power loading, kW/t/day (hp/ton/day)	0.34 (0.41)	0.34 (0.41)
Na_2S inlet, g/l	8.0-10.0	2.3-6.6
Na_2S outlet, g/l	0.01-0.05	0.01-0.10
Oxid. effic., % Na_2S	99^+	$98\text{-}99^+$
Oxygen ratio, act./theor.	7.7	14.2

9.1.2 Sieve Tray Towers

The Trobeck-Ahlen, Bergstrom-Trobeck, or Lundberg weak black liquor oxidation systems consist of countercurrent flows of air and liquor through a series of perforated sieve trays (15). The system is arranged in consecutive aeration and deaeration stages for consecutive air-liquor contact and air-liquor separation in series. The aeration stage consists of a seven-stage vertical sieve tray absorption tower where black liquor can be added at the third, fifth or seventh tray (numbered upward). The liquid is allowed to cascade downward from one tray to the next through a series of overflows and downcomers.

Air is introduced upward through the bottom of the tower and passes upward through the sieves, generating small gas bubbles and foam to facilitate interfacial gas-liquid contact. The liquor is drained from the oxidation tower into a deaeration tank. Sufficient retention time allows entrained gas bubbles to separate from the liquid. Mechanical foam breakers are used for foam control. The exhaust air stream from the oxidation tower passes through a cyclone separator for removal of entrained foam and liquor droplets. The system is illustrated in Figure 9-2.

Extensive experience has been obtained with sieve tray systems for weak black liquor oxidation in Europe, Canada, and the United States since 1942. Yemchuk (16) and Kacafirek (17) report Na_2S oxidation efficiencies from 85 to 95 percent with parallel operation of Trobeck-Ahlen weak black liquor oxidation towers. Sylwan (18) reports Na_2S oxidation efficiencies of up to 98 percent for a single tower Trobeck weak black liquor oxidation unit.

The higher oxidation efficiencies reported by Sylwan are at least partially the result of the greater air-to-liquor flow ratio of 36 m^3 air/m^3 black liquor (4.8 cu ft air/gal black liquor) as opposed to the lower values reported for the other systems of 15.0 m^3 air/m^3 black liquor (2.0 cu ft air/gal black liquor).

Blosser and Cooper (4) report on extensive experience with use of multiple tray-type black liquor oxidation towers at several kraft pulp mills in the United States. Relatively high Na_2S oxidation efficiencies of 96 to 99 percent are noted for all units without excessive foaming when the pine furnish is 20 percent or less. A summary of results is presented in Table 9-2.

Two recent installations, employing Trobeck-Ahlen weak black liquor oxidation systems, have been modified to prevent excessive foaming at mills pulping substantial quantities of pine wood species. Rippee (19) reports on a system for foam control at a western U.S. kraft mill pulping approximately 40 percent pine wood species (primarily ponderosa and western white). The liquid collected from the cyclone separator is drained to the tall oil recovery system instead of the deaeration tank. A portion of the strong black liquor is recycled to the inlet of the weak liquor oxidation tower to increase the solids concentration from 11 to 18 percent by weight. Approximately 20 percent of the liquor entering the tower is strong black liquor, resulting in a substantial decrease in foaming problems. Na_2S oxidation efficiency for the system has averaged 96 percent over an extended period.

Robinson (20) reports on modification of the design of a Trobeck oxidation unit to control foam at a southern U.S. kraft mill pulping about 70 percent pine wood species. A portion of the air is introduced at the tangential inlet of the cyclone separator to act as a piston for controlling the foam layer. The liquid stream passes through a series of deaeration tanks for further foam suppression and soap recovery. The Na_2S oxidation efficiencies have averaged approximately 98 percent over an extended period.

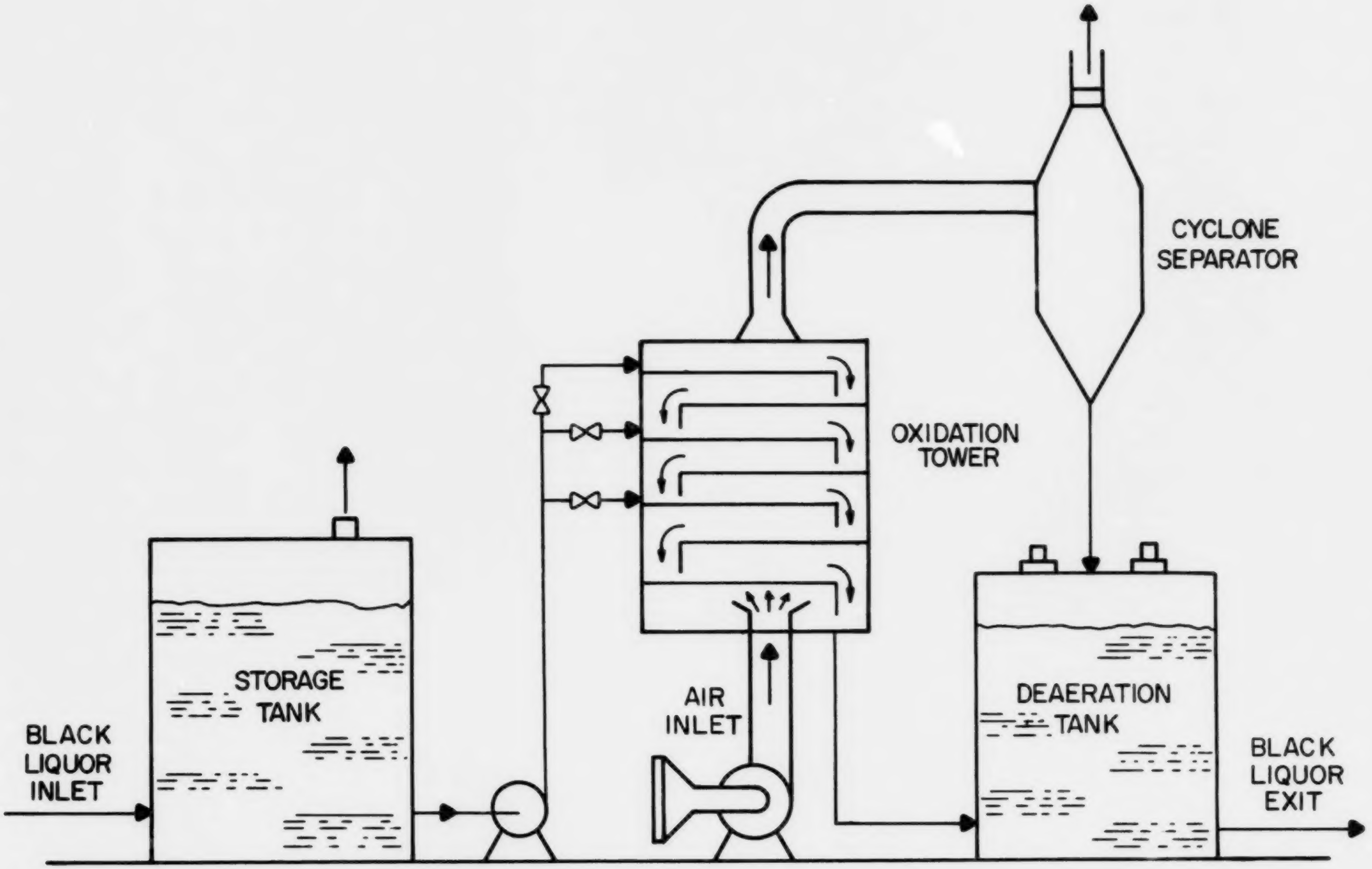

CYCLONE SEPARATOR
OXIDATION TOWER
STORAGE TANK
BLACK LIQUOR INLET
AIR INLET
DEAERATION TANK
BLACK LIQUOR EXIT

FIGURE 9-2

TROBECK-AHLEN MULTIPLE SIEVE TRAY WEAK BLACK LIQUOR OXIDATION SYSTEM (15)

TABLE 9-2

DESIGN AND OPERATING PARAMETERS FOR TROBECK-AHLEN MULTIPLE SIEVE TRAY WEAK BLACK LIQUOR OXIDATION UNITS (4)

Parameter	Mill A	Mill B	Mill C	Mill D
Liquor flow, m^3/h (gpm)	73 (320)	79 (350)	98 (430)	68 (300)
Air flow, m^3/h (cfm)	8,500 (5,000)	8,500 (5,000)	8,500 (5,000)	8,500 (5,000)
Plate area, m^2 (ft^2)	72 (780)	62 (665)	62 (665)	63 (672)
Na_2S loading, $Kg/m^2/h$ ($lb/ft^2/hr$)	6.3 (1.3)	8.3 (1.7)	11.2 (2.3)	12.2 (2.50)
Liquor loading, $m^3/m^2/h$ ($gal/ft^2/hr$)	1.0 (24.6)	1.3 (31.5)	1.6 (38.6)	1.1 (26.7)
Air loading, $m^3/m^2/h$ ($cu\ ft/ft^2/hr$)	118 (388)	137 (451)	137 (451)	135 (444)
Na_2S inlet, g/l	5.6	6.5	7.0	11.3
Na_2S outlet, g/l	0.03	0.2	0.3	0.1
Oxid. effic., % Na_2S	99	97	96	99
Oxygen ratio, act./theor.	14.3	12.7	16.8	19.0

9.1.3 Packed Towers

Packed towers are used for weak black liquor oxidation with air at kraft pulp mills in the Pacific Northwest with varying and somewhat limited effectiveness. The basic principle of operation is to provide gas-liquid contact by providing a large interfacial surface area through the use of packing instead of foam. Two different types of packed tower systems for weak black liquor oxidation with air have been developed, one by the Weyerhaeuser Company (21) (22) and the other by the British Columbia Research Council (23) (24).

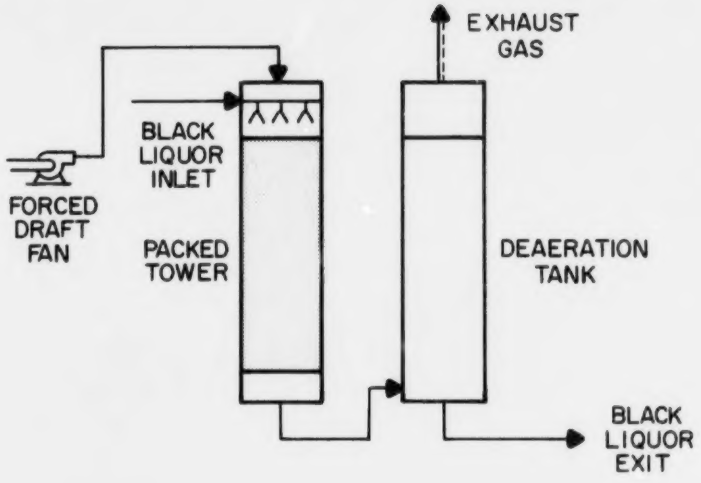
The Weyerhaeuser packed tower weak black liquor oxidation system uses concurrent downward vertical contact of air and black liquor in the tower to control foaming (25). The tower is packed with conventional packing materials to provide for gas-liquid interfacial contact area as shown in Figure 9-3. Design and operating parameters for several actual systems are presented in Table 9-3 (4).

The weak black liquor oxidation system of British Columbia Research Council introduces air and liquor concurrently at the top of parallel towers using successive layers of vertically layered packing sheets. The sheets allow wetting of both sides, and the spaces provide for lower pressure drops and resultant lower power requirements than do conventional packed tower configurations. Murray (25) reports that vertically layered asbestos packing sheet allows effective gas-liquid contact. West (26) observes that Na_2S oxidation efficiency approaches 100 percent at relatively low loading rates below 140 kg Na_2S per hour per m^2 of packing area (29 lb/hr per ft^2) when two oxidation towers are located in a series arrangement.

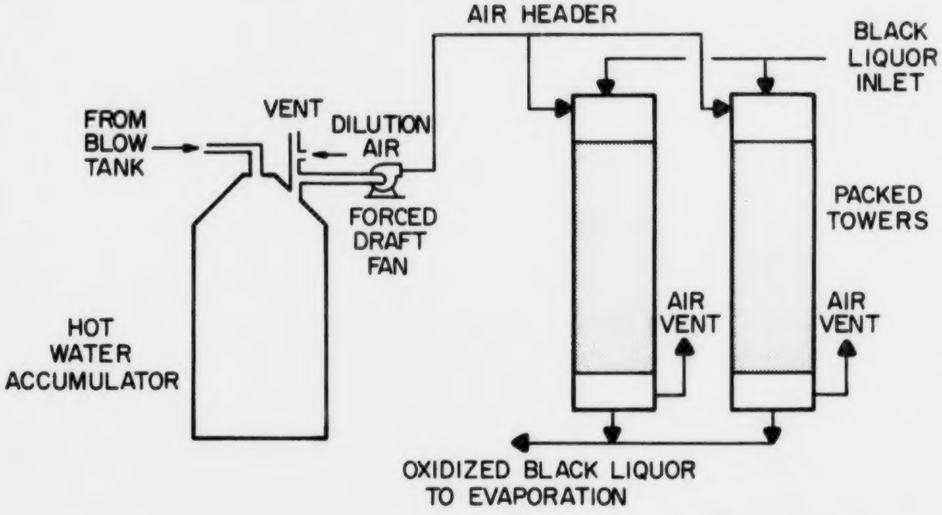
Packed towers are relatively simple devices to construct and operate, and they have minimal foaming problems and low horsepower requirements. They can be successfully operated when followed by a deaeration tank to prevent air entrainment in pumps. Most installations do not provide sufficient retention time for nearly complete oxidation of Na_2S to occur, have insufficient capacity for the pulp production rates involved, and are subject to plugging with pulp, particularly from continuous digesters.

9.1.4 Agitated Air Sparging

Agitated air spargers are used for weak black liquor oxidation at a few kraft pulp mills. The air sparger system employs a completely mixed tank containing weak black liquor with air dispersed through a turbine aerator at the bottom of the tank. A rotary agitator, located immediately above the aerator, shears the air into small bubbles to maximize the gas-liquid interfacial contact area. Additional power is provided to break the air into small bubbles instead of providing additional fan capacity and excess air. A typical unit is diagramed in Figure 9-4.


EXHAUST GAS
BLACK LIQUOR INLET
FORCED DRAFT FAN
PACKED TOWER
DEAERATION TANK
BLACK LIQUOR EXIT

WEYERHAEUSER SYSTEM (21)


AIR HEADER
BLACK LIQUOR INLET
FROM BLOW TANK
VENT
DILUTION AIR
FORCED DRAFT FAN
PACKED TOWERS
HOT WATER ACCUMULATOR
AIR VENT
AIR VENT
OXIDIZED BLACK LIQUOR TO EVAPORATION

BRITISH COLUMBIA RESEARCH COUNCIL SYSTEM (23)

FIGURE 9-3

PACKED TOWER SYSTEMS FOR WEAK BLACK LIQUOR OXIDATION

TABLE 9-3
DESIGN AND OPERATING PARAMETERS FOR WEYERHAEUSER CONCURRENT FLOW PACKED TOWER WEAK BLACK LIQUOR OXIDATION SYSTEM (4)

Parameter	Mill A	Mill B	Mill C	Mill D
Liquor flow, m^3/h (gpm)	102 (450)	68 (300)	238 (1,050)	127 (560)
Air flow, m^3/h (cfm)	6,100 (3,600)	17,000 (10,000)	11,400 (6,700)	10,800 (6,400)
Packing area, m^2 (ft^2)	12,900 (139,000)	13,950 (150,000)	22,000 (237,000)	35,000 (376,000)
Packing volume, m^3 (cu ft)	1,300 (46,000)	1,050 (37,200)	2,410 (85,000)	3,370 (119,000)
Tower height, m (ft)	7.0 (23)	11.0 (36)	13.1 (43)	11.0 (36)
Na_2S loading:				
Surface area, $kg/10^3 m^2/h$ ($lb/10^3 ft^3/hr$)	9.8 (2.0)	31.2 (6.4)	86.4 (17.7)	32.2 (6.6)
Volumetric, $kg/10^3 m^3/h$ ($lb/10^3 ft^3/hr$)	97.2 (6.0)	415.0 (25.9)	790.0 (49.2)	334.0 (20.8)
Liquor loading:				
Surface area, $m^3/10^3 m^2/h$ ($gal/10^3 ft^2/hr$)	7.9 (0.2)	4.9 (0.1)	10.8 (0.3)	3.6 (0.1)
Volumetric, $m^3/10^3 m^3/h$ ($gal/10^3 ft^3/hr$)	79 (0.6)	55 (0.4)	99 (0.7)	38 (0.3)
Air loading:				
Surface area, $m^3/m^2/h$ (cu $ft/ft^2/hr$)	0.47 (1.54)	1.22 (4.00)	0.52 (1.70)	0.31 (1.02)
Volumetric, $m^3/m^3/h$ (cu ft/cu ft/hr)	4.7 (4.7)	16.2 (16.2)	4.7 (4.7)	3.2 (3.2)
Na_2S inlet, g/l	1.20	6.40	8.00	8.90
Na_2S outlet, g/l	0.03	1.30	1.60	2.50
Oxidation efficiency, %	98	80	80	72
Oxygen ratio, act./theor.	33.0	25.0	3.9	6.2

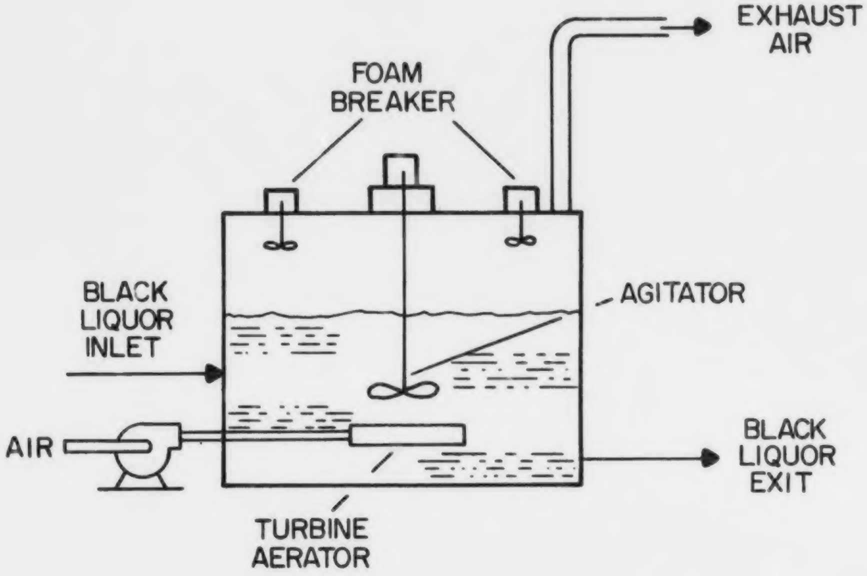

EXHAUST AIR
FOAM BREAKER
BLACK LIQUOR INLET
AGITATOR
AIR
BLACK LIQUOR EXIT
TURBINE AERATOR

FIGURE 9-4

AGITATED AIR SPARGING SYSTEM FOR BLACK LIQUOR OXIDATION

Two major problems noted with agitated air sparging units for weak black liquor oxidation are foaming caused by either low weak liquor solids content or by a wood furnish of greater than 10 percent pine (27) and mechanical breakdown of the liquid agitator system.

Methods employed for foam control are:

1. Placement of mechanical foam breakers at the top of the tank to break up stable foam, requiring 0.08 to 0.16 kW per metric ton per day (0.1 to 0.2 hp per short ton per day).

2. Use of chemical or kerosene defoamer in the black liquor,

3. Recycling of strong black liquor to the weak black liquor to increase the net liquid viscosity, and

4. Reducing retention time with resultant lowered oxidation efficiency. A summary of performance data for two units is presented in Table 9-4 (4).

TABLE 9-4
OPERATING AND PERFORMANCE DATA FOR AGITATED AIR SPARGED WEAK BLACK LIQUID OXIDATION SYSTEMS (4)

Parameter	Mill A	Mill B
Liquor flow, m^3/h (gpm)	243 (1,070)	262 (1,150)
Air flow, m^3/h (cfm)	8,500 (5,000)	4,250 (2,500)
Tank volume, m^3 (ft^3)	200 (7,060)	200 (7,060)
Retention time, min.	49	46
Na_2S loading, $kg/m^3/h$ ($lb/ft^3/hr$)	3.64 (0.23)	8.75 (0.55)
Liquor loading, $m^3/m^3/h$ ($gal/ft^3/hr$)	1.2 (9)	1.3 (10)
Air loading, $m^3/m^3/h$ ($ft^3/ft^3/hr$)	42.5	21.2
Na_2S inlet, g/l	3.0	6.7
Na_2S outlet, g/l	0.2	0.2
Oxidation efficiency, %	93	97
Oxygen ratio, act./theor.	8.0	2.6
Power required:		
Agitator, kW/t/day (hp/ton/day)	0.14 (0.17)	0.10 (0.12)
Foam breakers, kW/t/day (hp/ton/day)	0.16 (0.19)	0.10 (0.12)

9.1.5 Rotating Fluid Contactors

A limited amount of experience has been obtained with the Ashcroft dual vortex contactor, primarily in polishing weak black liquor to upgrade existing units. The system introduces weak black liquor tangentially into an axially downward flowing pipe of small diameter. Air is introduced to the liquid tangentially at the point where the small pipe connects with a wider pipe, resulting in large shearing forces and rapid gas-liquid mixing (28).

Preliminary results indicate that the system is suitable for weak black liquor oxidation with nonresinous wood species, but excessive foaming occurs for pine black liquor. One system employed to upgrade the performance of an existing weak liquor oxidation system feeds air into an Ashcroft unit at 5,000 m^3/h (3,000 cfm) with the black liquor flowing at 227 m^3/h (1,000 gpm). Installation of the unit results in increasing the overall Na_2S oxidation efficiency during weak black liquor oxidation from the former 50 to 60 percent to between 95 and 99 percent.

9.2 Strong Black Liquor Oxidation—Air

Strong black liquor oxidation with air, following multiple-effect evaporation, is employed at mills that pulp substantial quantities of resinous pine wood species to alleviate potential foaming problems, particularly in the southeastern United States. Strong black liquor oxidation reduces malodorous sulfur gas emissions from the direct contact evaporator and counteracts the tendency for Na_2S to reform. The major types of systems employed for strong black liquor oxidation are single- and two-stage unagitated air sparging. Agitated air spargers, plug flow reactors, and dual vortex contactors also are used for strong black liquor oxidation to a limited extent.

9.2.1 Single Stage Unagitated Air Sparging

The major technique employed for strong black liquor oxidation, to date, is a completely mixed unagitated air sparging tank. Hawkins (29) (30) describes the development of the original system at the Pasadena, Texas, mill of the Champion Paper Company. The system employs aeration and deaeration tanks arranged in series. The black liquor is oxidized by sparging with air in a single stage aeration tank, followed by separation of entrained air bubbles from the liquid in the deaeration tank. The aeration tank consists of a cylindrical section mounted between two conical sections, as shown in Figure 9-5.

Air is introduced in the bottom of the cylindrical section of the aeration tank through a series of eight radially branching sprayer arms in a Christmas tree arrangement. The sprayer arms are constructed of 20 cm (8 in) pipe with 19 nozzles for air outlet per branch and are connected to a central header. Each nozzle is 3.8 cm (1.5 in) in diameter. The air is caused to deflect downward against a deflector plate to achieve a fanning air curtain effect.

Air is introduced to the central header at a rate of 10,000 m^3/h (6,000 cfm). The exhaust air is drawn through a cyclone separator to remove entrained foam and liquor droplets, which are then returned to the aeration tank. The black liquor is introduced to the top of the tank through a 15 cm (6 in) diameter pipe located above the liquid level. The liquor is sprayed in from the bottom of the pipe through a series of 2.5 cm (1 in) holes evenly spaced along the pipe to obtain even liquid distribution and to provide a means for controlling foam. The black liquor is withdrawn from the bottom of the tank and passed to two deaeration tanks for gas-liquid separation to prevent pump malfunctions.

A Na_2S oxidation efficiency of 97 to 98 percent occurs at an inlet concentration of 30 g/l and at a liquid retention time of 2.5 hr. The process results in reducing H_2S emissions by 90 percent from the recovery furnace following direct evaporation as compared to H_2S emissions from unoxidized black liquor.

Blosser and Cooper (4) have prepared an extensive review of strong black liquor oxidation practices at kraft pulp mills. It is necessary to provide 3- to 5- times the stoichiometric amount of air for oxidation of Na_2S to sodium thiosulfate ($Na_2S_2O_3$). Air-to-liquid flow ratios must normally be greater than 110 to 190 m^3 air/m^3 strong black liquor (15 to 25 ft^3/gal of black liquor.) It is normally necessary to maintain a minimum liquor depth of 2.7 to 3.6 m (9 to 12 ft) with a minimum liquor retention time of 120 to 150 minutes to

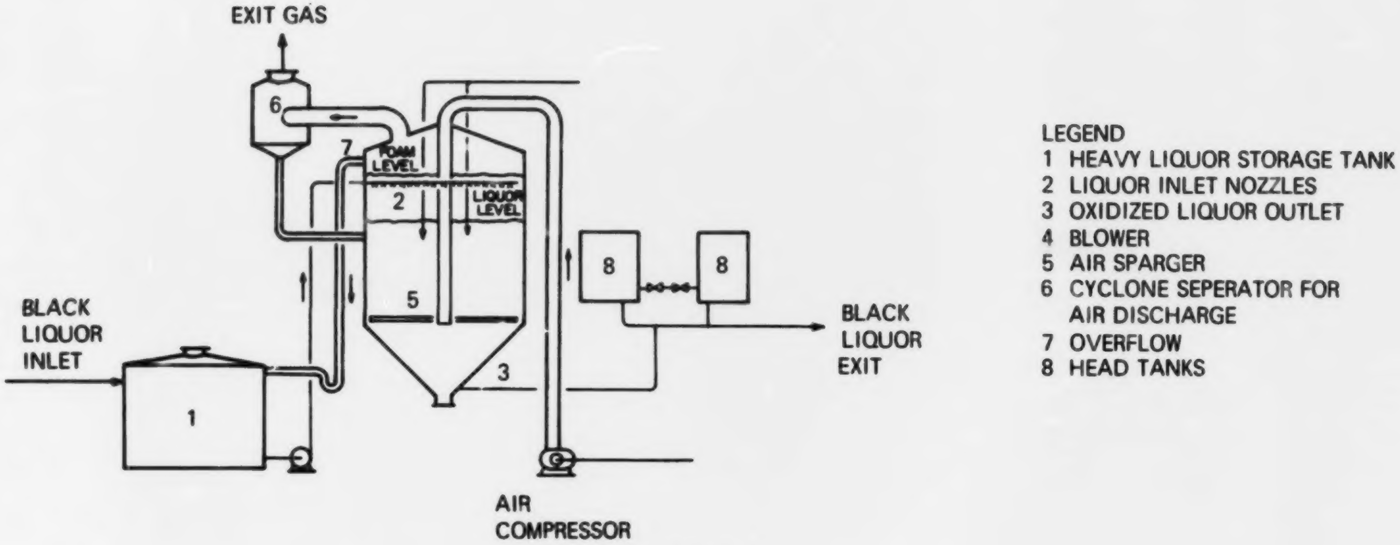

EXIT GAS
6
7
FOAM LEVEL
2
LIQUOR LEVEL
5
3
8
8
BLACK LIQUOR INLET
1
BLACK LIQUOR EXIT
AIR COMPRESSOR
LEGEND
1 HEAVY LIQUOR STORAGE TANK
2 LIQUOR INLET NOZZLES
3 OXIDIZED LIQUOR OUTLET
4 BLOWER
5 AIR SPARGER
6 CYCLONE SEPERATOR FOR AIR DISCHARGE
7 OVERFLOW
8 HEAD TANKS

FIGURE 9-5

CHAMPION UNAGITATED AIR SPARGE STRONG BLACK LIQUOR OXIDATION SYSTEM (29) provide for effective oxidation of the Na_2S. The product of the oxygen ratio (actual oxygen addition rate to theoretical oxygen addition rate) and liquor retention time in minutes must be 600 or greater to reduce exit Na_2S levels to less than 0.5 g/l in the oxidation tower exit liquid. The product of oxygen ratio and retention time must be greater than 1,000 to reduce Na_2S levels in the exit liquor to less than 0.2 g/l, as shown in Figure 9-6. These findings point to the possible development of two-stage systems for strong black liquor oxidation with air.

Morgan (31) (32) reports on the results of a study on a new strong black liquor oxidation system. He finds that the efficiency of strong black liquor oxidation is a function of liquor height, air flow rate, inlet Na_2S concentration, and retention time. The rate of Na_2S oxidation increases with increasing Na_2S concentration and air flow rate, decreasing retention time, and decreasing liquor height. Na_2S oxidation efficiencies of up to 99 percent are observed, but oxygen transfer efficiency is relatively low so that large quantities of excess air (3.5 times theoretical or more) are required to achieve high degrees of oxidation.

Foam control is particularly a problem during strong black liquor oxidation with air at kraft pulp mills in the southeastern United States. Several control methods are available. Effective soap removal during multiple-effect evaporation upstream of the oxidation unit removes

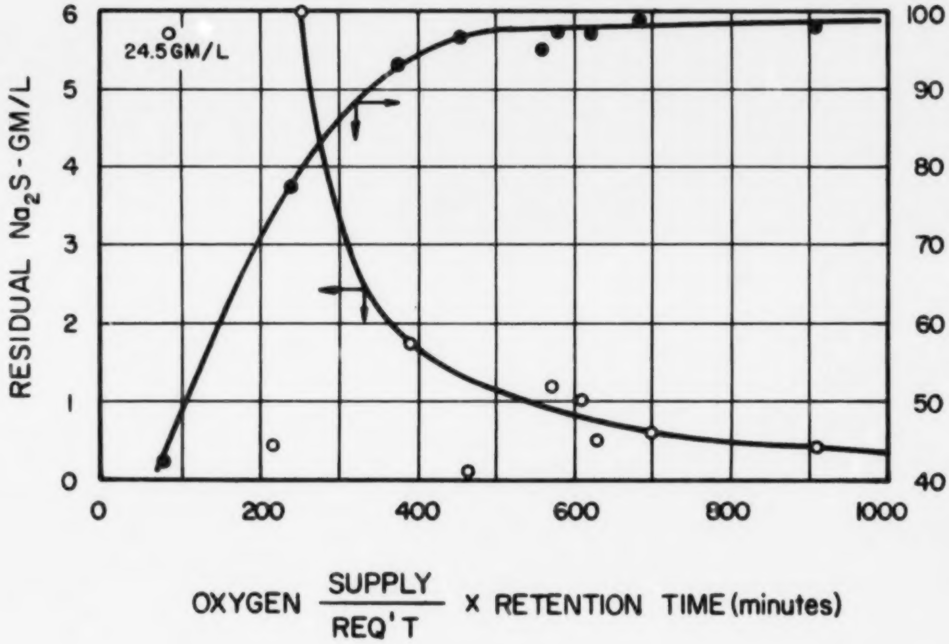


FIGURE 9-6

OPERATING & PERFORMANCE DATA FOR SINGLE STAGE STRONG BLACK LIQUOR OXIDATION SYSTEM (4) foam-producing materials (33). Cyclone separators in the exhaust gas line remove entrained foam and liquor droplets. Provision of adequate height above the liquor level allows for foam dissipation. Two to 5 m (6 to 15 ft) is the normal minimum required.

Mechanical and chemical methods of foam dissipation also are employed. Mechanical foam breaking requirements for strong black liquor oxidation systems are aeration tank only–0 to 0.022 kW per daily metric ton of pulp (0 to 0.027 hp/ton pulp per day) and aeration plus deaeration tank–0 to 0.007 kW per daily metric ton of pulp (0.0 to 0.1 hp/ton pulp per day). Chemical defoaming agents used include diesel oil and kerosene in dosages from 50 to 250 l/m^3 (50 to 250 gal/1,000 gal) strong black liquor, primarily on an intermittent basis. Mechanical foam breaking has not proved suitable in many cases where there are considerable foaming problems. The cost of chemical defoaming runs as high as $0.55 to $1.65/t ($0.50 to $1.50/ton) of pulp.

9.2.2 Two Stage Unagitated Air Sparging

Limitations in achieving Na_2S oxidation efficiencies above 99 percent to reduce exit concentrations of Na_2S to less than 0.1 g/l with single stage units have led to the development of multiple-stage strong black liquor oxidation systems. Padfield (34) reports on efforts to upgrade the single stage strong black liquor oxidation system from the former 97-98 percent Na_2S oxidation efficiency to a desired 99-100 percent. A second aeration tank of design similar to the first placed after the initial aeration tank provides for additional Na_2S oxidation. About a 60 minute retention time is provided in each oxidation tank with an additional 30 minutes of deaeration in the bottom of each tank to facilitate liquor pumping. The exit liquor from the second stage oxidation tank is sent directly to the direct-contact evaporators to prevent reversion to sodium sulfide.

The system has two air blowers for adding air to the black liquor, one for each tank. The blower for the first oxidation tank provides 10,400 m^3/hr (6,000 cfm) of air at 143 kPa total pressure (1.41 atmospheres or 6 psig) with a 187 kW (250 hp) motor. The blower for the second oxidation tank provides air at 8,500 m^3/hr (5,000 cfm) at the same pressure and using the same power. Two 19 kW (25 hp) mechanical foam breakers are required, one on each tank. Total power requirement for the two stage system is thus 410 kW (550 hp) for a pulp production of 770 Mg (850 tons) per day, or about 0.53 kW per daily metric ton of pulp (0.65 hp/ton/day). The system is illustrated in Figure 9-7 (34).

The average overall Na_2S oxidation efficiency for the system averages 99.95 percent, resulting in an average Na_2S concentration in the exit black liquor of 0.02 g/l. Emissions of H_2S from the recovery furnace are about 2 ppm by volume as compared to 50 ppm with the original single stage system.

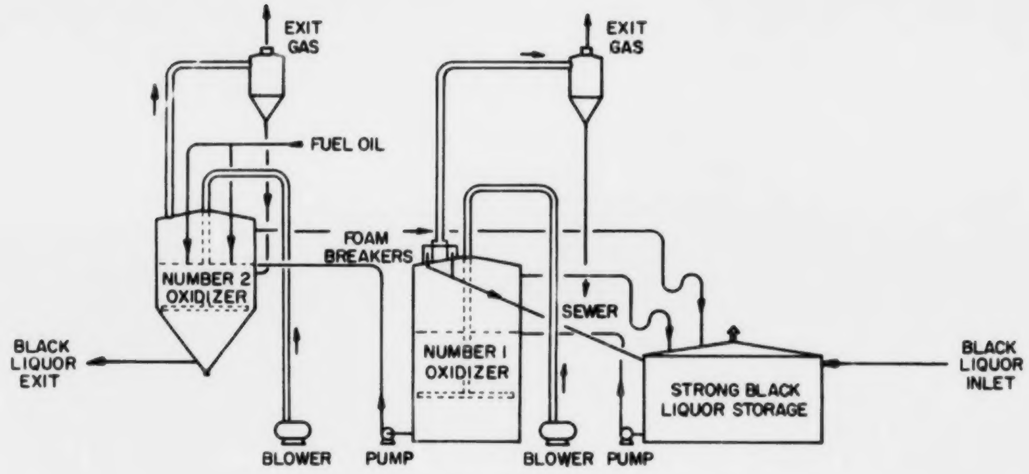


FIGURE 9-7

CHAMPION TWO STAGE UNAGITATED STRONG BLACK LIQUOR OXIDATION SYSTEM (34)

9.3 Agitated Air Sparging

The completely mixed agitated air sparging units employed for strong black liquor oxidation are of the same design as those described in section 9.1.4 for weak liquor systems. One unit introduces 10,400 m^3 air/h (6,000 cfm) into a black liquor flow of 80 m^3/h (350 gpm) at 48 percent solids using 150 kW (200 hp) agitated turbine aerator (4). The aeration tank has a diameter of 9.5 m (31 ft) and a height of 7.9 m (26 ft), and is operated at a liquid depth of 3.7 m (12 ft). Five 19 kW (25 hp) mechanical foam breakers are installed on the top of the unit, but have severe maintenance problems. No definitive results regarding efficiency of the unit are available because of the lack of sufficient operating experience. The system requires frequent maintenance because of agitator and foam breaker malfunctions.

9.4 Combination Systems

Tobias and Robertson (35) describe the development of an agitated concurrent plug-flow reactor system for oxidizing of strong black liquor with air. The primary purpose of the system is to polish the strong black liquor following multiple-effect evaporation to counteract the reversion to Na_2S of oxidized weak black liquor in an existing system. The system employs one oxidation unit on the exit pipe of the strong black liquor storage tank, and the other on the strong black liquor recirculation line, as shown in Figure 9-8. Each reactor is located so that a pipe with a central axially located baffle forms two mixing chambers, each with an agitator. Two parallel pipes are located immediately upstream of the agitators in both chambers, with holes drilled so as to obtain a fanning air curtain effect.

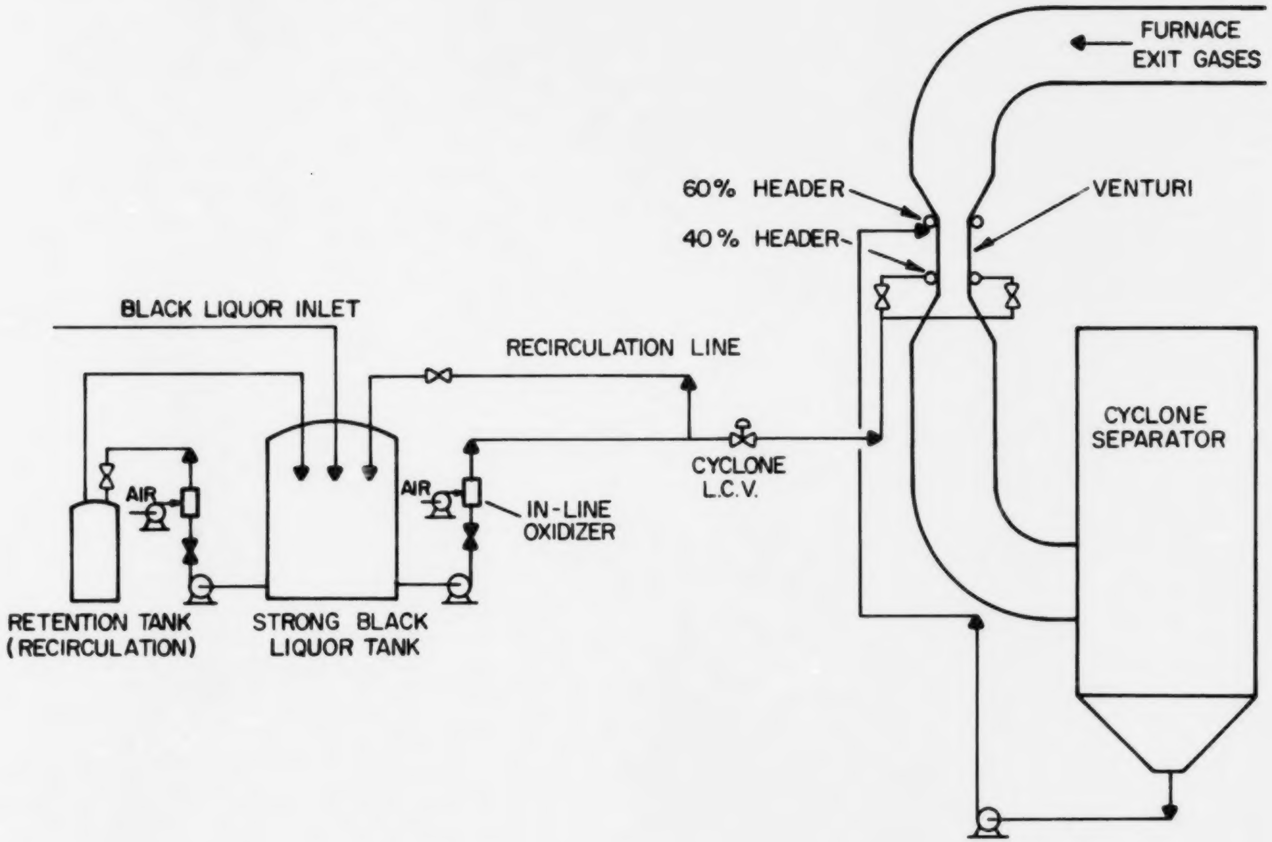

FURNACE
EXIT GASES
60% HEADER
40% HEADER
VENTURI
BLACK LIQUOR INLET
RECIRCULATION LINE
AIR
AIR
IN-LINE
OXIDIZER
CYCLONE
L.C.V.
CYCLONE
SEPARATOR
RETENTION TANK
(RECIRCULATION)
STRONG BLACK
LIQUOR TANK

FIGURE 9-8

WESTERN KRAFT PIPELINE REACTOR STRONG BLACK LIQUOR OXIDATION SYSTEM (35)

The air bubbles are sheared into smaller bubbles by the rotating action of the agitators to increase gas-liquid interfacial contact area, turbulence, and mixing.

Preliminary results indicate that the Na_2S oxidation efficiency for the system is virtually 100 percent with both units operating at inlet concentrations of 3 g/l or less. The oxidation efficiency is practically 100 percent with the system on the storage-tank exit line alone at Na_2S concentrations of 1.3 g/l or less. The system also appears to have higher oxygen utilization efficiencies than conventional air sparged units. No major problems with foaming are observed, but the wood furnish of the mill is primarily oak hardwoods. The two phase flow system reduces liquor line plugging but also causes substantial line vibration, requiring secure fastening of the pipes. When the system was installed at a second mill, the operation of the recovery furnace bed became unstable, possibly because of sulfate formation with resultant pH reduction and subsequent lignin precipitation from the black liquor.

Martin (36) describes reversion phenomena during multi-effect evaporation and also describes a secondary strong black liquor oxidation system installed downstream of an existing high efficiency weak black liquor oxidation unit. The system injects 680 m^3/h (400 cfm) of air into the bottom of an existing storage tank through a series of eight vertical pipes connected to a central header, where the black liquor flow is about 68 to 80 m^3/h (300 to 350 gpm). Results indicate that the Na_2S concentration of the black liquor entering the direct contact evaporator could be maintained at below 0.005 g/l with the inlet Na_2S concentration below 1.5 g/l.

9.5 Molecular Oxygen Systems

The severe foaming problems accompanying oxidation of weak black liquor with atmospheric oxygen (air) at kraft pulp mills pulping pine woods in the southeastern United States led to considering use of molecular oxygen as an alternative. The foaming problems of air oxidation can be alleviated by using molecular oxygen because the inert nitrogen-argon diluting medium is no longer present. The major drawback to using oxygen for black liquor oxidation has been its cost, but recent trends are toward lower oxygen prices, thus making it a more competitive alternative. Additional possible uses of oxygen include pulp bleaching, chemical pulping, wastewater treatment, and addition to recovery furnace firing zones for odor control. Such applications may lead to further increases in oxygen consumption at a given mill.

9.5.1 Preliminary Studies

Early laboratory investigations of Na_2S oxidation in black liquor with molecular oxygen have been made by Bergstrom and Trobeck (37), Venemark (38), Ricca (39), Sakhuja and Bosu (40), and Miller (41). Major findings of these laboratory studies are that the sulfide oxidation occurs in more than one rate-limiting regime, that $Na_2S_2O_3$ is the major reaction product, but that varying amounts of Na_2SO_4 are formed. The reaction rate is influenced by temperature and catalyzed by the presence of organic constituents in the black liquor. Cooper (42) reports on weak and strong black liquor oxidation with molecular oxygen in a series of pilot scale experiments. Design criteria are listed in Table 9-5 for plug flow reactor systems.

TABLE 9-5
DESIGN CRITERIA OF PLUG FLOW REACTOR SYSTEMS FOR BLACK LIQUOR OXIDATION WITH MOLECULAR OXYGEN (42)

Criteria	Weak Black Liquor Oxidation	Strong Black Liquor Oxidation
Performance:		
Na_2S efficiency, %	99^+	99^+
Na_2S outlet, g/l	0.01-0.02	0.01-0.02
Liquor:		
Reynolds number	100,000	10,000-20,000
Velocity, m/s (ft/sec)	1.5-4.5 (4.9-14.8)	1.0-3.0 (3.3-9.8)
Temperature, °C (°F)	77-88 (170-190)	110-115 (230-239)
Liquid pH	12.0-12.6	12.0-13.0
Solids, % by wt.	15-17	48-51
Oxygen:		
Oxygen ratio, Act/theoret.	1.1-1.3	1.2-2.5
Total pressure, atm	3.0-4.4	3.0-5.1
Partial pressure, % purity	90-99.5	90-99.5
Retention time (Liquor basis):		
Piping section, seconds	60-120	60-180
Storage tank, minutes	15-45	30-60

Both weak and strong black liquor oxidation systems employ plug flow reactors followed in series by tall storage tanks, as shown in Figure 9-9.

9.5.2 Weak Black Liquor Oxidation

Weak black liquor oxidation of lightly resinous pine black liquors with oxygen allows stabilization of Na_2S without causing the excessive foaming as with air. The process also has a lower capital cost than comparable air units because it can be carried out in a plug flow reactor within the piping of an existing mill. The use of oxygen would probably not

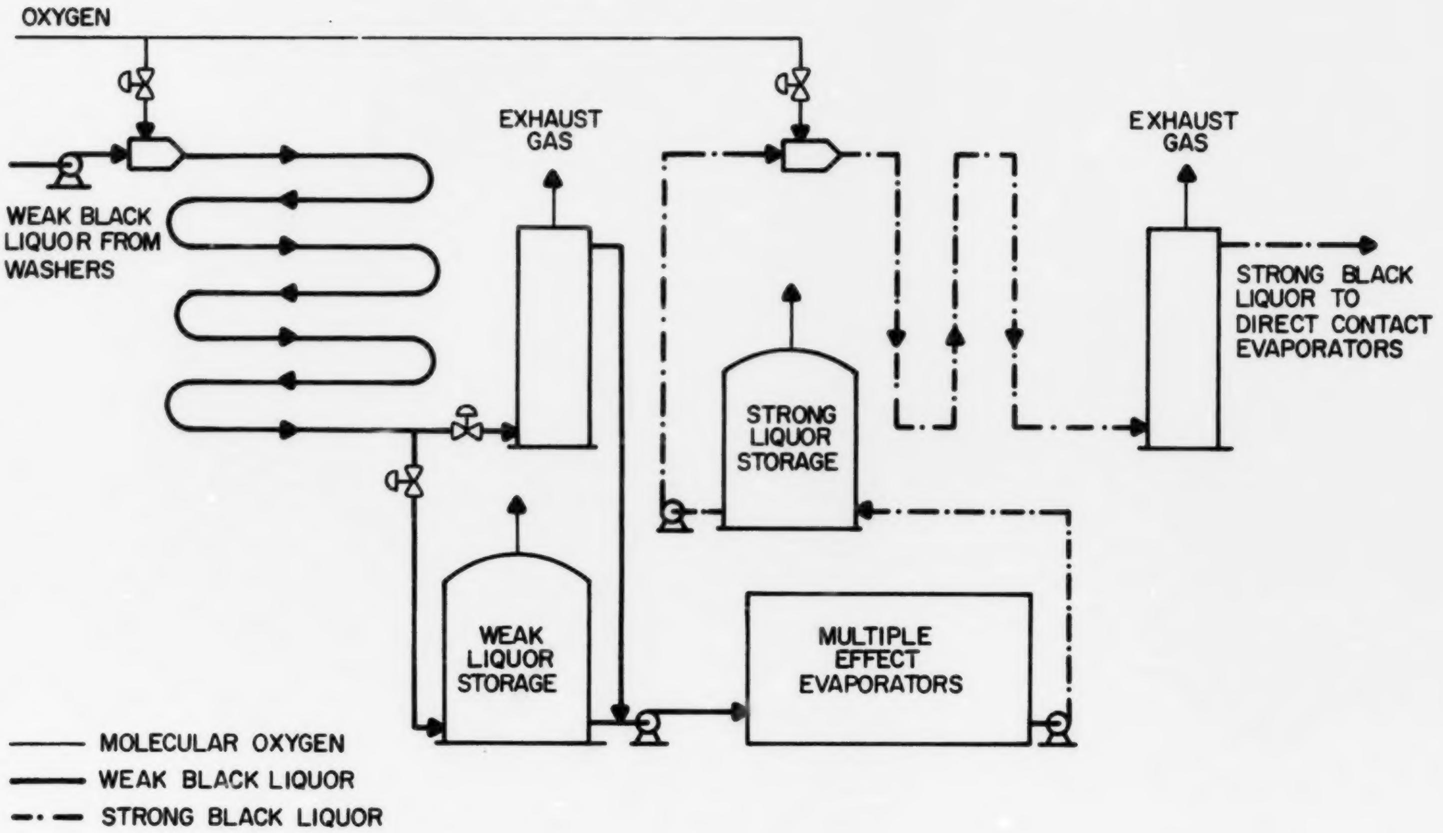

OXYGEN
WEAK BLACK LIQUOR FROM WASHERS
EXHAUST GAS
STRONG LIQUOR STORAGE
EXHAUST GAS
STRONG BLACK LIQUOR TO DIRECT CONTACT EVAPORATORS
WEAK LIQUOR STORAGE
MULTIPLE EFFECT EVAPORATORS
MOLECULAR OXYGEN
WEAK BLACK LIQUOR
STRONG BLACK LIQUOR

FIGURE 9-9

TWO STAGE COMBINATION WEAK & STRONG BLACK LIQUOR OXIDATION WITH OXYGEN overcome the problems of Na_2S reversion in oxidized black liquor unless the process were carried out at a temperature above 130° C (266° F).

Kosaya (43) describes the first reported use in 1956 of molecular oxygen for weak black liquor oxidation at the Kehra pulp mill in the Soviet Union. The system was originally installed to reduce the H_2S emission from multiple-effect evaporators, with the aim of improving the water quality and reducing odor. The pulp mill was a kraft mill that did not use recovery furnace flue gas for direct contact evaporation. The system injects oxygen into the black liquor upstream of the multiple effect evaporators through a "dosing apparatus." Results indicate that it is possible to achieve "essentially complete" oxidation of the Na_2S in the black liquor at an inlet concentration of 7.5 g/l within "several minutes of retention time" in the pipe at a temperature of 70° C (158° F). No problems with foaming were observed, and absorption of oxygen in the pipeline reactor was virtually complete.

The study indicates that the oxygen consumption is about 12 percent greater than the stoichiometric amount for conversion of Na_2S to $Na_2S_2O_3$, as shown in Table 9-6. An overall finding is that oxidation of weak black liquor with molecular oxygen is potentially attractive from an economic standpoint.

TABLE 9-6
OXYGEN REQUIREMENTS FOR WEAK BLACK LIQUOR OXIDATION* (43)

Dimension	Theoretical	Actual
m^3 of O_2/t of Na_2S	315	370
(cu ft of O_2/ton of Na_2S)	(10,080)	(11,850)
kg of O_2/t of pulp	24	58
(lb of O_2/ton of pulp)	(48)	(116)
m^3 of O_2/m^3 of black liquor**	2.1	2.5
(cu ft of O_2/gal of black liquor)	(0.28)	(0.33)

*Black liquor conditions: 15% solids, 7.54 g Na_2S/l.
**Based on black liquor flow of 8 m^3/t pulp (1900 gal/ton pulp).

Freedman (28) reports on the oxidation of weak black liquor with molecular oxygen in 1970, when an Ashbrook rotating cyclonic fluid contactor was used to provide contact between the oxygen and black liquor. The system introduces black liquor tangentially into a small diameter pipe and redirects its flow axially to form a centrifugal cyclonic liquid flow pattern. Oxygen is then introduced tangentially into the liquid at the point of concentric expansion into a larger diameter pipe. The violent mixing of the fluids causes a large number of small oxygen bubbles to form. Collectively, these bubbles will provide a large interfacial contact area between the gas and the liquid.

Pilot studies, using the contactor for oxidation of weak black liquors with oxygen, indicate that effective oxidation of Na_2S can be achieved with liquors from both northern hardwoods and southern pine woods. Excessive foaming does not occur in either case because of the absence of the argon-nitrogen diluent from the incoming gas stream. Essentially complete oxidation of sodium sulfide can be obtained within 15 to 60 seconds for hardwood black liquors, and within about 60 seconds for southern pine black liquors. Oxygen usage efficiencies of 85 to 90 percent are obtained in both cases, making the technique economically favorable. The exothermic oxidation also warms the black liquor by up to 10° C (18° F), thus decreasing evaporator stream heating requirements.

Galeano and Amsden (44) report on an extensive study of using molecular oxygen tor weak black liquor oxidation at the Owens-Illinois, Inc. kraft pulp mill in Orange, Texas, where southern pine wood species are primarily pulped. Basically, the system introduces molecular oxygen into a flowing stream of black liquor in a two-step pipeline reactor with a retention time of 15 to 40 seconds, followed by tank storage with a retention time of 8 to 12 hours.

Oxygen gas enters the 61 cm (24 in) diameter horizontal inlet pipe at a total pressure of 0.45 MPa (50 psig) at a flow rate of 850 to 1,360 m^3/h (500 to 800 cfm) through an injector oriented perpendicular to the liquid. It is broken up into small bubbles under high turbulence by a venturi effect. The black liquor enters the inlet pipe at a flow rate of 227 to 386 m^3/h (1,000 to 1,700 gpm) with a Na_2S concentration of 9 to 12 g/l, a solids content of 12 to 15 percent, and a temperature of 93 to 100° C (200 to 230° F). After contacting the oxygen, the black liquor flows through a 30 m (100 ft) length of 25 cm (10 in) diameter pipe, where the oxygen is absorbed and the Na_2S oxidized. The initial contact section provides for a liquid Reynolds number of 100,000 to 200,000 in highly turbulent flow. The system is diagramed in Figure 9-10.

Galeano and Amsden observed Na_2S oxidation efficiencies of 85 to 98 percent (94 average) without excessive foaming with an oxygen usage efficiency of 75 to 95 percent (91 average). About 90 percent (of the total 94 percent) of the Na_2S is oxidized to $Na_2S_2O_3$ within the pipeline reactor section. There is a subsequent conversion of about 15 percent of the $Na_2S_2O_3$ to Na_2SO_4, as listed in Table 9-7.

Not all the sulfur is accounted for by the above chemical analyses alone, indicating either the formation of other products, such as polysulfide, sulfite, or polythionate ions, or loss by gasification. The initial Na_2S oxidation reaction is extremely rapid. Additional changes in

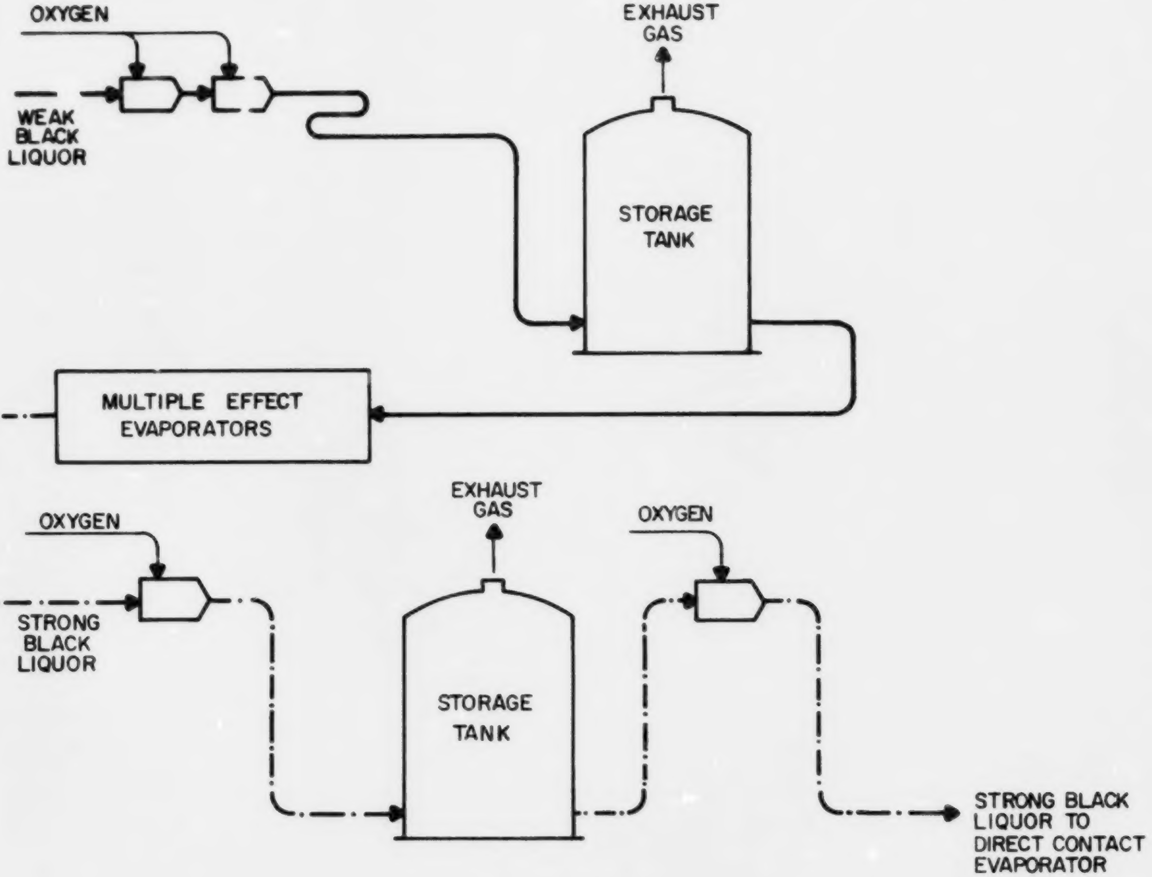

OXYGEN
WEAK BLACK LIQUOR
EXHAUST GAS
STORAGE TANK
MULTIPLE EFFECT EVAPORATORS
OXYGEN
STRONG BLACK LIQUOR
EXHAUST GAS
STORAGE TANK
OXYGEN
STRONG BLACK LIQUOR TO DIRECT CONTACT EVAPORATOR

FIGURE 9-10

OWENS-ILLINOIS SYSTEM FOR TWO STAGE WEAK & STRONG BLACK LIQUOR OXIDATION WITH OXYGEN (45)

TABLE 9-7
EFFECT OF WEAK BLACK LIQUOR OXIDATION ON LIQUID CHEMICAL COMPOSITION (44)

Location	Chemical Component				Account
	Na_2S g/l	$Na_2S_2O_3$ g/l	Na_2SO_4 g/l	Total g/l	%
Reactor inlet	4.56	0.80	0.53	5.89	100.0
Reactor outlet	0.45	4.35	0.70	5.50	93.7
Storage outlet	0.19	4.61	0.63	5.43	92.8

black liquor during the oxidation process are a rise of 0.1 to 0.3 pH units because of thiosulfate formation, and a temperature rise of 5 to 8° C (10 to 15° F) caused by the exothermic oxidation.

Galeano and Amsden observed several benefits of weak black liquor oxidation with molecular oxygen as compared to lack of oxidation, namely:

1. H_2S emissions during direct contact evaporation declined by 95 to 99 percent during multiple-effect evaporation,
2. Na_2SO_4 makeup requirements declined by 30 kg/t pulp (60 lb/ton pulp),
3. Evaporator condensate water quality improved, and
4. Tall oil yield increased by about 15 percent.

The effects of weak black liquor oxidation on sulfur gas emissions from various process sources are listed in Table 9-8.

The mill is located adjacent to an oxygen pipeline where the low oxygen cost of $9.35/t of O_2 ($8.50/ton) results in a maximum net mill operating cost of $0.06 to $0.09 per metric ton of pulp ($0.05 to $0.08/ton). Projected capital costs for similar oxygen generating installations are $55 to $83 per daily metric ton of pulping capacity ($50 to $75 per daily short ton).

TABLE 9-8
EFFECT OF WEAK BLACK LIQUOR OXIDATION ON SULFUR GAS EMISSIONS FROM KRAFT MILL PROCESS SOURCES (44)

Source	Constituent	Concentration Unoxidized ppm, by vol.	Concentration Oxidized ppm, by vol.	Reduction %
Cyclone evaporator exit	H_2S	191	10	95
	RSH	161	5	97
	RSR + RSSR	20	0	100
	SO_2	243	241	1
Weak black liquor storage tank vent	H_2S	553	3	99
	RSH	760	375	50
	RSR	1,274	280	78
Evaporator noncondensable gas vent	H_2S	1,208	4	99
	RSH	>>500	300	>50
Evaporator condensate	Sulfide	72	28	60
	BOD	863	530	38

9.5.3 Strong Liquor Oxidation

Very little work has been devoted to the use of molecular oxygen for strong black liquor oxidation. Galeano and Amsden (45) describe the use of strong black liquor oxidation with oxygen for polishing to counteract reversion to Na_2S from the previously oxidized weak black liquor. The system introduces the oxygen into the strong black liquor in an expanded pipe section at two places. The black liquor then flows downward to take advantage of the gas bubble "holdup" phenomenon with its attendant increased effective retention time, and then through a horizontal pipe section to a strong black liquor storage tank. The liquid Reynolds number in the pipeline reactor ranges from 10,000 to 20,000 in the liquid at 53 percent solids, at a temperature of 120° C (250° F), and with a liquid retention period of 30 to 50 seconds.

Initial studies indicate potential problems with black liquor cooling, lignin oxidation, and incomplete oxygen mass transfer into the black liquor, resulting in incomplete Na_2S oxidation. Little Na_2S reversion in the oxidized weak black liquor is observed, possibly because of the high inlet temperatures, 93 to 110° C (200 to 230° F), of liquor from the continuous digesters. The liquid retention time in each pipeline reactor stage is about one minute. The result is a reduction in the Na_2S concentration in the strong black liquor from 1.5 g/l to between 0.05 and 0.10 g/l.

9.5.4 Digester Injection

It is possible to introduce oxygen into the kraft recovery system at the digester at the end of the cook. Oxidation of the Na_2S and sodium mercaptide (NaHS) at the end of the cook prevents gaseous conversion and release of these compounds into the atmosphere. The technique has the advantages of performing the oxidation in an enclosed reactor, thus assuring complete use of the oxygen added, and performing the operation at high temperatures to assure maximum reaction rates and minimal possibilities for reversion to Na_2S. The technique can also result in oxidation of organic sulfur compounds to prevent their discharge and to limit emissions from the digester, washers, multiple-effect evaporators, tall oil and storage tank vents, and the direct contact evaporators.

Possible digester corrosion and excessive oxygen consumption can possibly occur because of competing side reactions, such as sulfate formation and lignin oxidation and potential degradation in pulp quality. Two studies investigated addition of molecular oxygen to kraft mill digesters at the ends of cooks to oxidize the Na_2S and NaHS present in the black liquor.

Fones and Sapp (46) report on the addition of oxygen to a kraft digester to oxidize black liquor in 1960. Oxygen is added at the ends of successive cooks to a pressure vessel containing pulp alone, black liquor alone, and a mixture of pulp and black liquor. For the test cook with pulp alone, the lignin content of the pulp is reduced by oxidation, and its brightness is increased.

When oxygen is injected into a digester containing both pulp and black liquor at the end of the cook, the Na_2S is rapidly and completely oxidized. The high reaction temperatures and pressures result in the formation of substantial quantities of Na_2SO_4 with a resultant drop in liquid pH and a sharp increase in the amount of oxygen consumed. In addition, the oxidation process also reduces the bursting strength and brightness of the pulp, and its lignin content. Oxidation of the black liquor with oxygen at the end of the cook is uneconomical because of the excessive oxygen requirements and the detrimental effects on pulp quality.

Tests were made to determine the effect of oxygen addition on the oxidation of Na_2S in a pressurized vessel containing only black liquor. Oxygen was added to black liquor alone in a digester at a total pressure of 0.8 MPa (100 psig) and 150° C (302° F) in a series of stages to recirculated black liquor. The oxygen then reacted with the Na_2S and other constituents until the pressure returned to its initial value in a time span of four hours. Results indicate that the initial reaction product was $Na_2S_2O_3$, but substantial quantities of Na_2SO_4 were also present causing a resultant drop in liquid pH. Because oxygen consumption was about double that for stoichiometric conversion of Na_2S to $Na_2S_2O_3$, the process proved prohibitively expensive with oxygen costing $22/t ($20/ton).

Kringsted and McKean (47) describe oxidation of Na_2S and NaHS in black liquor at the end of a draft cook in the presence of pulp. Their results indicate that by oxygen addition to a kraft digester at the end of a cook, the Na_2S concentration in black liquor can be reduced by 90 percent and NaHS by 99 percent but twice the stoichiometric amount of oxygen is required.

An additional finding is that no sodium polysulfide or Na_2SO_3 could be detected in the black liquor during the oxidation period, indicating that it might be possible to reduce or eliminate potential problems caused by reversion to Na_2S. No measurements for Na_2SO_4 were made during the tests.

The process does not affect the pulp strength or yield, but does make the pulp easier to beat and also reduces its brightness. Oxygen addition to a digester at the end of a kraft cook can effectively oxidize Na_2S and NaHS, and can minimize potential problems caused by reversion. Of particular importance is that the relatively long retention time of about 20 minutes at a high temperature of approximately 180° C (356° F) can result in the possible oxidation of substantial amounts of $Na_2S_2O_3$ to Na_2SO_4, and also of lignin. The nonselective oxidation process can require excessive quantities of oxygen in assuring oxidation of the Na_2S and NaHS, thus making the process economically unattractive.

9.6 Process Effects

Black liquor oxidation influences the operation of the kraft chemical recovery system in other ways in addition to reducing malodorous sulfur gas emissions. Major influences include:

1. Improvement in multiple-effect evaporation through reduced scaling on heat transfer surfaces,
2. Reduced corrosion rates of metal evaporating surfaces,
3. Possible increases in tall oil yield,
4. Reduced chemical makeup requirements for Na_2SO_4 and calcium oxide (CaO),
5. Possible increases in green and white liquor sulfidities, with resultant effects on pulp yield and quality, and
6. Possible effects on black liquor heating values.

9.6.1 Evaporator Scaling

Berry (48) finds that the H_2S evolved from unoxidized weak black liquor causes the formation of an iron sulfide (FeS) scale, which inhibits the rate of heat transfer in the multiple-effect evaporators. The precipitation of lignin on the heat transfer surfaces can be minimized by maintaining a sufficiently high liquid pH, thus alleviating another potential source of evaporator scaling. Any Na_2SO_4 formed during weak liquor oxidation becomes less soluble as liquid temperature increases and can cause a scaling problem during the latter stages of evaporation at higher solids concentrations.

9.6.2 Corrosion During Evaporation

Weak black liquor oxidation can substantially reduce the corrosion of multiple-effect evaporator surfaces, particularly in the vapor shell sections. Von Essen (49) reports that the corrosion of evaporator surfaces is caused primarily by the formation of FeS from H_2S in a moist atmosphere on metal surfaces. The rate of corrosion is reduced by about 85 percent by reducing the inlet Na_2S concentration in black liquor to less than 3 g/l. Cyr and Harper (50) report that the average life of multiple-effect evaporator tubes is substantially increased by weak black liquor oxidation.

9.6.3 Tall Oil Yield

Weak and strong black liquor oxidation can increase tall oil yields for byproduct recovery by either physical or chemical mechanisms (33). Foaming, however, could be a serious problem with air oxidation of pine black liquors where large quantities of tall oil are obtained. Galeano and Amsden (44) report that tall oil yield is increased by approximately 15 percent as the result of weak black liquor oxidation with molecular oxygen. Also, there is no apparent decrease in tall oil quality and there are increases in yield of as much as 7.5 to 12.5 kg per metric ton of pulp (15 to 25 lb/ton). Rippee (19) reports an approximate 10 percent increase in tall oil yield at a western U.S. kraft pulp mill achieved by oxidizing weak black liquor with air and recycling strong black liquor for foam control. At a 1972 National Council symposium (51), black liquor oxidation was reported to result in increased tall oil yields. But the quality of the tall oil decreased, possibly because of its oxidation.

9.6.4 Chemical Recovery

Black liquor oxidation reduces the sulfur losses from kraft process sources, resulting in decreased Na_2SO_4 and lime chemical makeup requirements. Galeano and Amsden (44, 45) report that to maintain a given sulfidity level the Na_2SO_4 makeup rate can be reduced by 15 to 30 kg per metric ton of pulp (30 to 60 lb/ton) of pulp. To provide a portion of the sodium makeup requirements, NaOH can be used. The lime makeup requirement can be reduced by 1.0 to 1.5 kg per metric ton of pulp (2-3 lb/ton), and the total lime mud processing rate can be reduced by 5.0 to 7.5 kg per metric ton of pulp produced (10 to 15 lb/ton). Specific chemical savings for maintaining particular sulfidity levels will vary between mills.

9.6.5 Liquor Sulfidity

A major effect of black liquor oxidation on the kraft pulping process is the increase in green and white liquor sulfidities. The reason for the increased sulfidity levels is the retention of additional sulfur in the recovery system; less H_2S is lost to the recovery furnace flue gas stream during the direct contact evaporation (52). The increase in green liquor sulfidity results in a decrease in both lime makeup and lime burning requirements, with a resultant decrease in fuel requirements at the lime kiln (44).

Black liquor oxidation can result in increased white liquor sulfidity levels of two to five percent or more for a given Na_2SO_4 chemical makeup rate, or a reduction of 15 to 30 kg per metric ton of pulp (30 to 60 lb/ton) to maintain a given sulfidity level (14). The increased white liquor sulfidity levels can increase the rate of delignification during digestion of wood chips. The greater sulfidities also can increase the emission of malodorous organic sulfur compounds from digester blow and relief gases, brown stock washer vents, and multiple-effect evaporator gases (53).

Shah and Stephenson (14) observed that the installation of weak black liquor oxidation results in a 2- to 5-percent increase in white liquor sulfidity for given chemical makeup rates. Increases in pulp quality and yield were observed during the digestion process, but they probably are offset, at least in part, by increased corrosion caused by higher Na_2S levels. The increased sulfidity may cause increased malodorous sulfur gas emissions from the kraft recovery system because of the higher sulfur circulation rates.

One drawback to the usage of black liquor oxidation is that it can cause the inlet Na_2S concentrations in the black liquor to rise sharply, thus overloading the oxidation capacity of the existing system. Ritchey (54) reports that installation of a strong liquor oxidation system using air at an existing mill resulted in about a 50 percent increase in the inlet Na_2S concentration in the unit, that is, from about 40 to 60 g/l. The equivalent sulfidity increase was approximately 10 percent, resulting in a reduction in Na_2S oxidation efficiency from the expected 98 percent to about 80 percent. To maintain proper sodium-sulfur ratios in the recovery system it is necessary to add NaOH as part of the sodium makeup.

9.6.6 Energy Balances

Black liquor oxidation affects energy conservation in the kraft recovery system. Lime kiln fuel requirements are reduced with increasing liquor sulfidity levels (see section 9.6.5). Oxidation of black liquor results in a reduction in net heating value of black liquor because of the oxidation of both the reduced sulfur compounds and the organic lignin fuel materials. Losses in heating value can range from 2 to 6 percent (55). The oxidation of black liquor can act to maintain cleaner heat transfer surfaces, thus reducing steam requirements during multiple-effect evaporation. With air oxidation there is a slight evaporation of water, which acts to concentrate the solids. But the effect can be offset for air by liquor cooling, particularly for strong black liquor.

The oxidation of kraft black liquor increases the efficiency of heat transfer by reducing multiple-effect evaporator scaling. Weak black liquor oxidation with air increases the liquor solids concentration by 1 to 2 percent by weight because of the water evaporated, thus reducing steam and fuel requirements. Freedman (28) observes that weak black liquor oxidation with pure oxygen results in a warming of the black liquor by 10° C (18° F), thereby reducing the sensible heat requirements during multiple-effect evaporation. There are several potentially detrimental effects. Miller (41) observed during a series of pilot scale studies that oxidation with molecular oxygen caused a cooling of strong black liquor. Tomlinson and Douglas (22) note that the endothermic heat requirements for reduction of $Na_2S_2O_3$ and Na_2SO_4 in the kraft recovery furnace can result in slightly lower heat release and lower subsequent steam generation for use in digestion and evaporation sections. The decreased heat release could cause possible increases in supplementary fuel costs.

Roberson (56, 57) observed that weak black liquor oxidation with air reduced its heating value by about 2 percent, with a resulting decreased heat release. Lindholm and Stockman (55) find that weak black liquor oxidation with molecular oxygen reduced the liquor heating value by 2.0 and 3.6 percent for Na_2S oxidation efficiencies of 90 and 100 percent, respectively. The loss in heating value is caused primarily by oxidation of organic matter, resulting in increased oxygen consumption and decreased heat availability. Cooper (58) observes that black liquor oxidation with oxygen can decrease the heating value of weak black liquor by 2 to 4 percent, and strong black liquor by 6 to 8 percent.

9.7 Air Pollution Effects

Weak black liquor oxidation has several beneficial effects on reducing malodorous sulfur gas emissions from several sources, including the multiple-effect evaporator noncondensable gases, tall oil vents, storage tank vents, and the direct contact evaporator of the recovery furnace. Weak black liquor oxidation also can result in improvement of evaporator condensate water quality to facilitate process water reuse. Strong black liquor oxidation results in a reduction in malodorous sulfur gas emissions from direct contact evaporation, but does not provide any of the benefits for multiple-effect evaporation as does weak black liquor oxidation. Black liquor oxidation with air creates an additional source of odorous gas emissions. These emissions are practically negligible when molecular oxygen systems are employed.

9.7.1 Direct Contact Evaporation

Direct contact evaporation is used at most kraft pulp mills to concentrate black liquor from 50 percent solids to 60-65 percent solids. Direct contact evaporation may liberate malodorous sulfur gases on contact of liquor with recovery furnace flue gas because the CO_2 of the flue gas may acidify the lignin sufficiently to generate H_2S from Na_2S. Black liquor oxidation can minimize reduced sulfur gas emissions from the direct contact evaporator by oxidizing Na_2S to stable products in the liquid.

Major variables affecting the emission rate of malodorous sulfur gases are inlet Na_2S and NaHS concentrations, liquor pH, and degree of gas-liquid contact. Murray (59) observes that increasing the black liquor pH above 12.0 causes a substantial decrease in H_2S emission from recovery furnaces following direct contact evaporation. Increasing the degree of gas-liquid contact by increasing the pressure drop at high liquor firing rates can increase total reduced sulfur (TRS) emissions from the direct-contact evaporator.

The primary variable affecting H_2S emission from the direct-contact evaporator is the Na_2S concentration of the incoming black liquor. Oxidation of the Na_2S and NaHS to innocuous products in either weak black liquor upstream or strong black liquor downstream can substantially reduce malodorous sulfur gas emissions. This reduction is particularly significant for the multiple-effect evaporator noncondensable gases, tall oil vent gases, and recovery furnace flue gases, and also evaporator condensates. The substantial reduction in sulfur gas emissions from direct-contact evaporation is shown in Table 9-9.

Due to their growing relative significance, organic sulfur emissions from direct contact evaporation will also be important to consider as more stringent emission standards are adopted. Methyl mercaptan (CH_3SH) is oxidized in the presence of oxygen to CH_3SSCH_3, which has a lower odor threshold level. CH_3SCH_3 and CH_3SSCH_3 can be removed by the

TABLE 9-9
EFFECT OF BLACK LIQUOR OXIDATION ON SULFUR GAS EMISSIONS DURING DIRECT CONTACT EVAPORATION (60)

Sulfur Compound	Liquor			
	Unoxidized		Oxidized	
	kg S/t	(lb S/ton)	kg S/t	(lb S/ton)
H_2S	2.50-15.00	(5.0-30)	0.05-1.00	(0.1-2.0)
CH_3HS	0.15-1.00	(0.30-2.0)	0.02-0.10	(0.04-0.2)
CH_3SCH_3	0.02-0.08	(0.04-0.16)	0.01-0.03	(0.02-0.06)
CH_3SSCH_3	0.05-0.15	(.1-.3)	0.01-0.08	(0.02-0.16)

stripping action of the flue gases. The degree of removal depends on the inlet concentrations in the liquid, the liquid and gas temperatures, and the pressure drop across the direct contact evaporator. Polishing with oxygen at temperatures of 120 to 140° C (250 to 285° F) may be necessary to oxidize the organic sulfur constituents in strong black liquor and, therefore, prevent their release to the atmosphere.

9.7.2 Evaporator Noncondensable Gases

Weak black liquor oxidation has substantially reduced H_2S and CH_3SH emissions from evaporator noncondensable gases, according to Douglass (61), Reid (62, 63), and Galeano (44). The sulfur gas emissions are reduced by increasing black liquor pH and decreasing inlet Na_2S and NaHS concentrations. The effect of weak black liquor oxidation on malodorous sulfur gas emissions from multiple-effect evaporator noncondensable gases is presented in Table 9-10 (60).

TABLE 9-10
EFFECT OF WEAK BLACK LIQUOR OXIDATION ON
MALODOROUS SULFUR GAS EMISSIONS FROM
EVAPORATOR NONCONDENSABLE GASES (60)

Sulfur Compound	Liquor			
	Unoxidized		Oxidized	
	kg S/t	(lb S/ton)	kg S/t	(lb S/ton)
H_2S	0.05-1.40	(0.10-2.8)	0.00-0.01	(0-.02)
CH_3SH	0.05-0.50	(0.10-1.0)	0.05-0.10	(0.1-0.2)
CH_3SCH_3	0.01-0.02	(0.02-0.04)	0.01-0.04	(0.02-0.08)
CH_3SSCH_3	0.00-0.01	(0.0-0.02)	0.02-0.05	(0.04-0.10)

9.7.3 Evaporator Condensate Waters

The oxidation of weak black liquor results in reducing the amounts of malodorous sulfur gases liberated for subsequent absorption in the evaporator condensate waters. As reported by Kosaya (43) and Chisoni (64), two European mills employ weak black liquor oxidation primarily to control odor levels in evaporator condensate waters and to gain, as a side effect, control of water pollution.

Three additional studies have been made regarding the effect of weak black liquor oxidation on evaporator condensate water quality. Shah and Stephenson (14) find that the installation of a weak black liquor oxidation system reduced the BOD of the condensate water by 27 percent and substantially reduced the odor level. The liquid pH is raised from 6.5 to 9.0, making the evaporator condensate water suitable for process reuse as brown stock washer makeup water. Galeano and Amsden (44) note a 38 percent reduction in BOD and 60 percent reduction in sulfide ion concentration with weak black liquor oxidation using molecular oxygen at a southern U.S. kraft mill.

Turner and Van Horn (65) find that CH_3OH contributes 64 percent of the total BOD of evaporator condensate water from evaporating unoxidized black liquor at a southern kraft mill. Galeano and Amsden (44) speculate that one reason for the decrease in BOD of the condensate water is the partial oxidation of CH_3OH to formaldehyde (HCHO) during weak black liquor oxidation, along with the reduction in sulfide ion concentration. Weak black liquor oxidation may promote reuse of evaporator condensate water by reducing the treatment required for recycling.

9.7.4 Tall Oil Vent Gases

The oxidation of weak black liquor reduces the inlet Na_2S concentration of the liquid supplied to the tall oil recovery system; the H_2S liberated during acidulation of the tall oil proportionately declines. Little information is available on sulfur gas emissions from tall oil processing.

9.7.5 Storage Tank Vents

Black liquor oxidation can reduce the emission of H_2S and CH_3SH from storage tank vents. Galeano and Amsden (44) report reductions of 99 percent for H_2S, 50 percent for CH_3SH, and 78 percent for organic sulfides from the storage tank vents following weak black liquor oxidation with oxygen.

9.7.6 Ambient Air Quality

Hendrickson and Harding (3) observe that the installation of parallel strong black liquor oxidation systems substantially reduces the malodorous sulfur gas concentrations in the ambient air near the mill. The ambient level of odorous gas concentrations, as measured by "reducible sulfur" concentration (a general indicator of H_2S levels), was 50 to 75 percent lower after installation of black liquor oxidation facilities.

9.8 Oxidation Tower Emissions

Black liquor oxidation facilities can reduce sulfur gas emissions from the direct contact and multiple-effect evaporators, tall oil vents, and storage tanks. The use of weak or strong black liquor oxidation with air does provide an additional source of reduced sulfur compounds to the atmosphere. Reduced sulfur emissions from tank vents where black liquor is oxidized with molecular oxygen are negligible in comparison to those from air oxidation systems because the nitrogen-argon diluent is no longer present to cause any stripping.

Primary factors affecting sulfur gas emissions from black liquor oxidation tower vents when air is used for oxidation are the inlet concentrations in the black liquor, the temperature of the black liquor, the height of the black liquor in the tank, and the air flow rate per unit volume. Sulfur gas emissions tend to increase for higher liquid temperatures and for greater air flow rates because of the greater volatility of warmer gases and the stripping action of the air. Sulfur gas emissions also tend to increase with increasing inlet concentrations in the incoming black liquor. Use of hardwood species or contaminated condensates for brown stock washer makeup can be the cause of increased inlet concentration.

The primary sulfur gas constituents present in black liquor oxidation tower exhaust are organic sulfur compounds, such as CH_3SCH_3 and CH_3SSCH_3. In addition, other volatile organic nonsulfur constituents can be stripped from the black liquor, such as terpenes, alcohols, and hydrocarbons. The emissions from weak and strong black liquor oxidation systems are summarized in Table 9-11 (66).

TABLE 9-11
REDUCED SULFUR EMISSIONS FROM BLACK LIQUOR OXIDATION TOWER VENTS USING AIR (66)

Condition	Weak Black Liquor		Strong Black Liquor	
	kg S/daily t	(lb S/daily ton)	kg S/daily t	(lb S/daily ton)
Average	0.06	(0.11)	0.05	(0.10)
Minimum	0.01	(0.02)	0.005	(0.01)
Maximum	0.11	(0.22)	0.09	(0.18)

Large volumes of exhaust gases with high moisture content are generated during black liquor oxidation. These gases can be incinerated in large boilers that have sufficient combustion capacity, provided that safety precautions are taken to accommodate the wet gases. Hisey (67) describes a system at a kraft pulp mill in South Africa where exhaust gases from the black liquor oxidation tower are added to the primary air inlet of the recovery furnace. This is the only installation known to date to employ this technique.

9.9 Process Economics

Two recent surveys of capital and operating costs were made for weak and strong black liquor oxidation systems that use air (4) (56). The weak systems normally have higher capital costs than the strong ones for equivalent production because of greater liquid volume at lower solids concentration. The strong liquor oxidation systems normally have higher operating costs than the weak ones of equivalent production because a greater amount of energy is required for oxygen mass transfer into the viscous strong liquor.

9.9.1 Air Oxidation Systems

Calculations by Roberson (56, 57) verify the higher capital and operating costs for strong black liquor oxidation systems than for equivalent weak ones. Roberson's design features for a hypothetical processing mill were an inlet Na_2S concentration of 6.0 g/l in the weak black liquor or the equivalent in strong liquor concentration, and a Na_2S oxidation efficiency of 99 percent across the system. Results of the calculations are shown in Figure 9-11.

Blosser and Cooper (4) present a compilation of capital and operating costs for existing weak and strong black liquor oxidation systems from data supplied by individual mills. Capital cost figures are adjusted to a base of December 1968 from reported values to correct for the effects of inflation and are listed in Table 9-12.

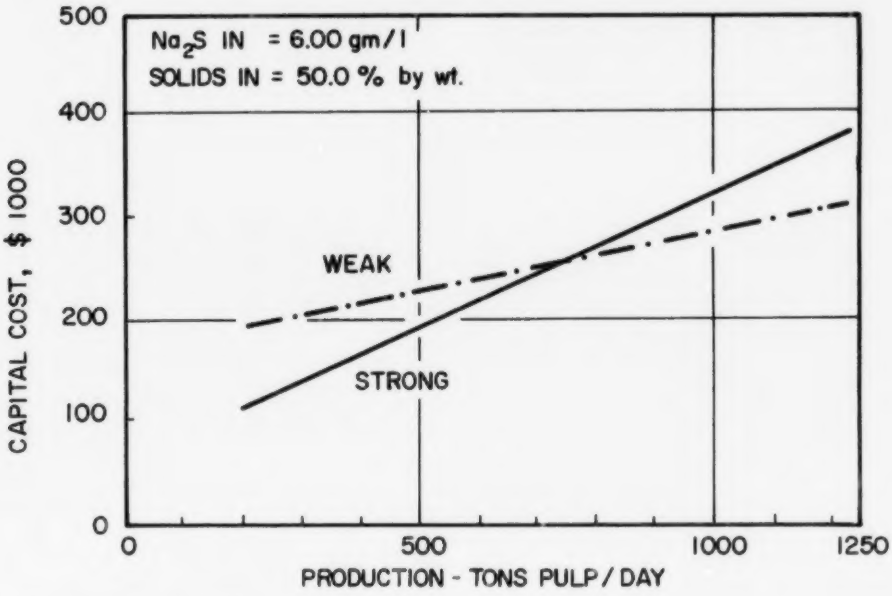
TABLE 9-12
ESTIMATED CAPITAL COSTS FOR BLACK LIQUOR
OXIDATION SYSTEMS

Unit Description		Installation Cost*		Reference
Location	Type	$/daily t	($/daily ton)	
Weak	Packed tower	440-660	(400-600)	4
	Multiple tray	440-880	(400-800)	4
	Agitated sparger	330-385	(300-350)	4
	Rotating fluid	55-165	(50-150)	28
Strong	Unagitated sparger	300-770	(275-700)	4
	Agitated sparger**	440-660	(400-600)	4
	Plug flow reactor**	6-55	(5-50)	35

*Adjusted basis of December 1968.
**Estimated values.

Annual operating costs for black liquor oxidation systems depend on a number of variables. The major component expense is for electric power, but equipment maintenance, interest

A. CAPITAL COST



B. OPERATING COST

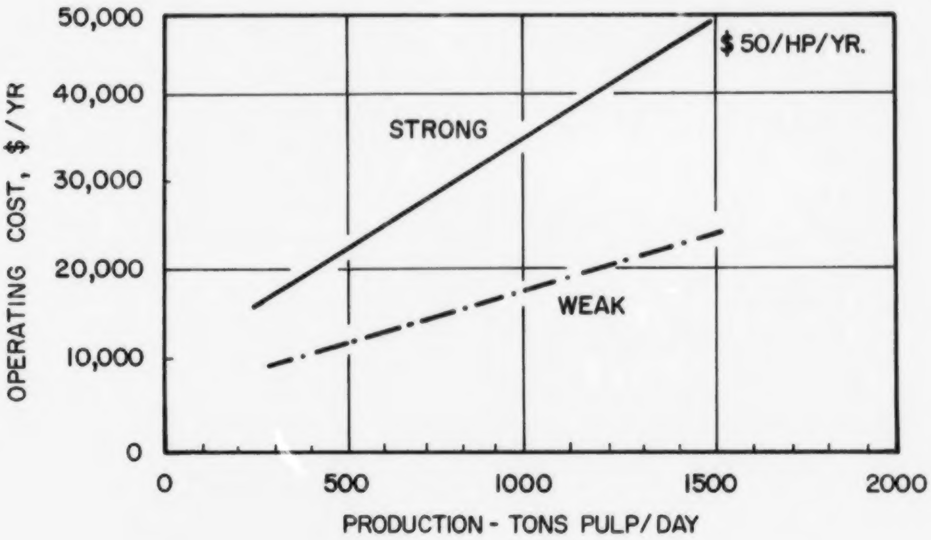


FIGURE 9-11

EFFECT OF PRODUCTION RATE ON CAPITAL & OPERATING COSTS FOR WEAK & STRONG BLACK LIQUOR OXIDATION WITH OXYGEN (56) on invested capital, and depreciation must also be included. A summary of direct annual operating costs for black liquor oxidation systems is presented in Table 9-13.

TABLE 9-13
APPROXIMATE ANNUAL OPERATING COSTS FOR BLACK LIQUOR OXIDATION SYSTEMS USING AIR

Black Liquor	Power Requirement		Operating Cost*	
	kW/daily t	hp/daily ton	$/daily t	$/daily ton
Weak	0.16-0.49	0.2-0.6	11-55	10-50
Strong	0.41-0.82	0.5-1.0	22-220	20-200

*Does not include operating cost credits.

Operating variables for systems include inlet Na_2S concentration; liquor depth in the tank; auxiliary facilities, such as foam breakers and agitators; and the possible need for chemical addition for foam control or pH adjustment. An additional factor is whether a system is single- or multiple-staged. Sheppard (68) reports a 30 percent decrease in annual operating costs in converting from a single- to a double-stage strong black liquor oxidation system, as listed in Table 9-14.

TABLE 9-14
EFFECT OF NUMBER OF STAGES ON ANNUAL OPERATING COSTS FOR STRONG BLACK LIQUOR OXIDATION WITH AIR (68)

Number of Stages	Flow		Power		Annual Operating Cost	
	m^3/h	(cfm)	kW	(hp)	$/daily t	($/daily ton)
1	76,500	(45,000)	2,720	(3,650)	100.50	(91.15)
2	41,000	(24,000)	1,870	(2,500)	69.25	(62.81)
3	35,800	(21,000)	1,810	(2,430)	67.00	(60.77)

9.9.2 Molecular Oxygen Systems

The capital costs for black liquor oxidation systems using molecular oxygen are considerably lower than for air oxidation systems. This is because molecular oxygen processing can be carried out within the piping of an existing mill without constructing large separate tanks. Galeano and Amsden (44) estimate the cost for two stage weak black liquor oxidation system at $55 to $83 per metric ton of installed daily capacity ($50 to $75 per ton/day) and the cost for strong black liquor polishing at $83 to $165 per metric ton of installed daily capacity ($75 to $150 per ton/day). Cooper (58) estimates capital costs for black liquor oxidation with oxygen, depending on the materials of construction used, as listed in Table 9-15.

The primary factors affecting operating costs for strong black liquor oxidation with oxygen are the inlet Na_2S concentration and the oxygen unit purchase cost. Normally, 15 to 25 percent excess oxygen must be added to provide for maximum Na_2S oxidation efficiency. An additional 5 to 10 percent more oxygen than that required for weak black liquor oxidation alone must also be added for strong black liquor polishing. The effect of oxygen unit costs and inlet Na_2S concentration on unit operating costs for weak black liquor oxidation with oxygen is presented in Figure 9-12 (66). A summary of calculated ranges in operating cost credits and debits for black liquor oxidation with oxygen is presented in Table 9-16 (69).

A summary of estimated operating parameters, reduced sulfur emissions, and capital and operating cost values for weak and strong black liquor oxidation with air and oxygen is presented in Table 9-17.

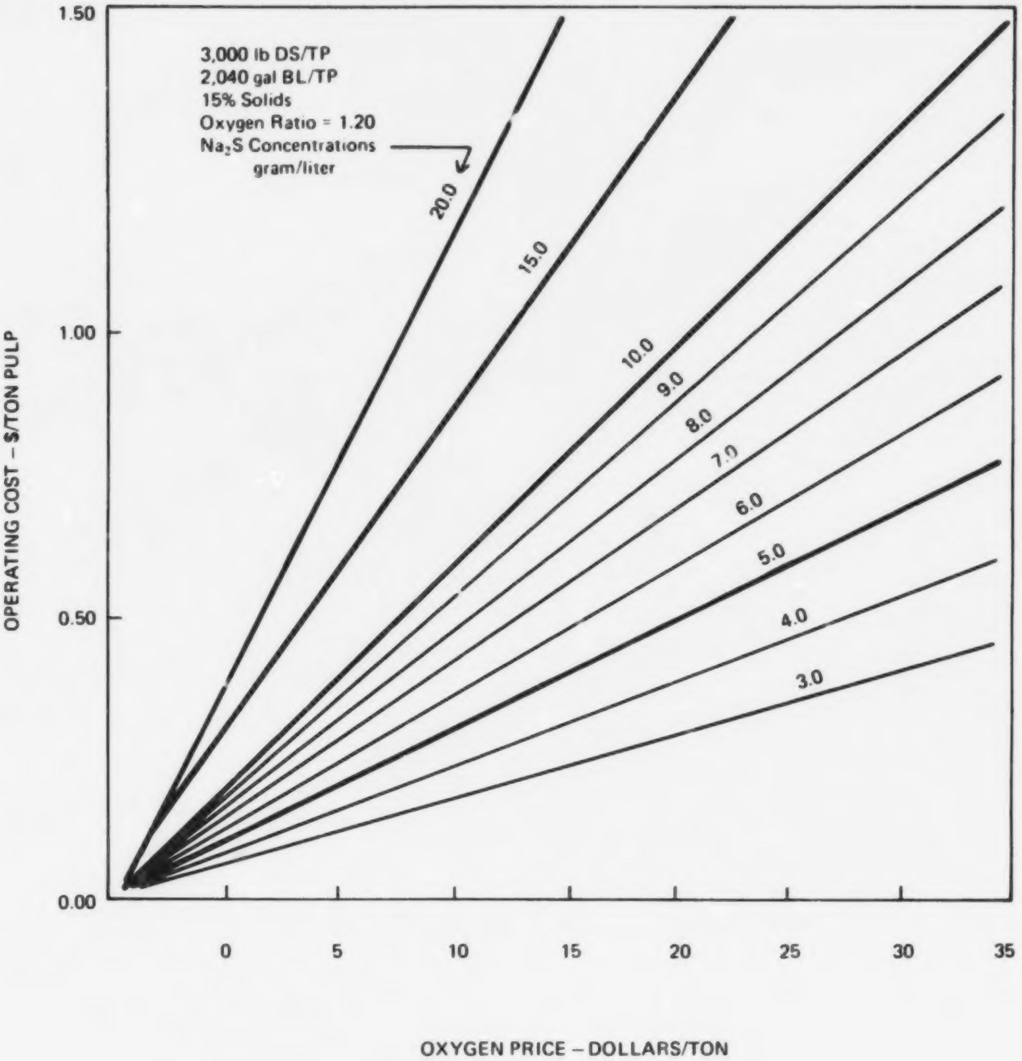


FIGURE 9-12

OPERATING COSTS FOR WEAK BLACK LIQUOR OXIDATION WITH OXYGEN (66).

TABLE 9-15
ESTIMATED CAPITAL COSTS FOR BLACK LIQUOR OXIDATION SYSTEMS USING MOLECULAR OXYGEN*

	Weak Liquor System		Strong Liquor System	
Reactor Section	Carbon Steel	Stainless Steel	Carbon Steel	Stainless Steel
	(All costs in $/daily t ($/daily ton))			
Liquid pumping	2-3 (2-3)	2-3 (2-3)	1-2 (1-2)	1-2 (1-2)
Oxygen injection	1-2 (1-2)	1-2 (1-2)	1-3 (1-3)	1-3 (1-3)
Piping section**	2-6 (2-5)	13-17 (12-15)	3-6 (3-5)	6-11 (5-10)
Storage tank	11-22 (10-20)	28-55 (25-50)†	6-11 (5-10)	14-28 (13-25)††
Total	16-33 (15-30)	44-77 (40-80)	11-22 (10-20)	22-44 (20-40)

*Cost data from Popper, H. (ed.). Modern Cost Engineering & Techniques. New York, McGraw-Hill Book Co., 1970. p. 80-178.

**Liquid retention times of 30 to 60 seconds.

†Liquid retention times of 15 to 30 seconds.

††Liquid retention times of 30 to 60 seconds.

TABLE 9-16
OPERATING COSTS AND OPERATING CREDITS FOR BLACK LIQUOR OXIDATION WITH OXYGEN (69)

Cost or Credit	Item	Amount	Cost/Credit Range \$/t (\$/ton)
Cost	Oxygen:		
	Weak Black Liquor	10-60 kg O_2/t (20-120 lb O_2/ton)	0.11-1.65 (0.10-1.50)
	Strong Black Liquor	0.5-7.5 kg O_2/t (1-15 lb O_2/ton)	0.01-0.28 (0.01-0.25)
Cost	Electric Power	0.04-0.12 kW per t/day (0.05-0.15 hp per ton/day)	0.01-0.03 (0.01-0.03)
Cost	Operating and Maintenance	0.5-1.0 h/wk	0.01-0.02 (0.01-0.02)
Total Costs			0.14-1.98 (0.13-1.80)
Credit	Tall Oil Yield	0-13 kg/t (0-26 lb/ton)	0.0-1.10 (0.0-1.05)
Credit	Sodium Sulfate	0-15 kg/t (0-30 lb/ton)	0.0-0.33 (0.0-0.30)
Credit	CaO	0.5-2.5 kg/t (1-5 lb/ton)	0.01-0.06 (0.01-0.05)
Credit	Kiln fuel savings	3-10%	0.03-0.11 (0.03-0.10)
Total Credits			0.04-1.66 (0.04-1.50)

TABLE 9-17

TYPICAL RANGES IN OPERATING VARIABLES, REDUCED SULFUR EMISSIONS AND COST FACTORS FOR BLACK LIQUOR OXIDATION SYSTEMS (69)

	Air Oxidation Systems			Molecular Oxygen Systems			
Item	WBLO* Only	SBLO** Only	WBLO & SBLO	Digester Only	WBLO Only	SBLO Only	WBLO & SBLO
Operating Variables:							
Oxygen reqm't., act/theor.	4-6	5-8	7-10	2-3	1.1-1.3	1.4-1.7	1.2-1.5
Power reqm't., kW/daily	0.2-0.8	0.4-1.2	0.6-1.5	0.1-0.2	0.02-0.08	0.02-0.04	0.04-0.12
(hp/daily ton)	(0.3-1.0)	(0.5-1.5)	(0.7-1.8)	(0.1-0.3)	(0.03-0.10)	(0.02-0.05)	(0.05-0.15)
Na_2S to direct contact evaporator, g/l	0.3-1.5	0.02-0.1	0.01-0.5	0.05-0.5	0.3-1.5	0.1-1.0	0.01-0.10
Na_2S oxidation efficiency, %	97-99	95-99	99-99$^+$	90-99	98-99	96-98	99-100
Reduced Sulfur Emissions:							
Evaporator gases, kg/t	0.05-0.5	0.5-5.0	0.05-0.5	0.025-0.25	0.05-0.25	0.05-5.0	0.05-0.25
Tall oil vent, kg/t	0.05-0.1	0.5-0.75	0.05-0.1	0.025-0.1	0.025-0.1	0.5-0.75	0.05-0.1
BLO tower vent, kg/t	0.05-0.25	0.05-0.15	0.05-0.3	0	0-0.01	0.-0.005	0.025-0.25
Recovery furnace, direct contact evaporator, kg/t	0.1-1.5	0.05-1.0	0.05-0.5	0.025-0.5	0.05-1.5	0.1-1.5	0.05-0.25
Economic Factors:							
Capital cost, $/daily t	330-880	550-880	660-1100	11-55	27-137	55-220	55-165
($/daily ton)	(300-800)	(500-800)	(600-1000)	(10-50)	(25-125)	(50-200)	(50-150)
Annual operating cost, $/daily t	11-110	27-220	55-275	33-550	11-330	22-440	17-385
($/daily ton)	(10-100)	(25-200)	(50-250)	(30-500)	(10-300)	(20-400)	(15-350)

*WBLO = Weak Black Liquor Oxidation.
**SBLO = Strong Black Liquor Oxidation.

9.10 References

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CHAPTER 10

RECOVERY BOILER DESIGN AND OPERATION

10.1 General Conditions

10.1.1 Process Parameters Outside Recovery Boiler

Recovery boilers are used for the combustion of spent liquor from the following sodium-base pulping processes:

1. Sodium sulfate (kraft)
2. Sodium bisulfite, and
3. Neutral sulfite semi-chemical (NSSC) in combination with kraft.

The kraft process can be used for making paper grade pulp or, when combined with a prehydrolysis stage, this process can be used to make dissolving pulp. The pH of the bisulfite process can range from acidic to alkaline at the finishing stage of the cooking. The NSSC process also has a certain pH range.

The amount of black liquor and its characteristics depend to a great extent on the type of pulping used (owing to differences in the cooking liquor and the pulp yield), the species of wood used for pulping and the site of the growth of the wood.

The part of the wood no longer present in the pulp after cooking is converted to:

1. Organic and inorganic components in the dry solids in the black liquor;
2. Volatile compounds, such as terpenes, CH_3OH, CO_2;
3. Soap and waxes; and
4. Water.

The organic part of the black liquor dry solids can be classified as lignin derivatives and carbohydrates. Lignin contains more carbon and less oxygen than the carbohydrates. The hydrogen content is almost the same for both. The compositions of softwood lignin and hardwood lignin are slightly different. The heat values and oxygen demand for combustion differ for the different compounds (1) (2).

Part of the volatile compounds, the soaps and the waxes may be present in black liquor when it reaches the recovery boiler for combustion. Part of these components may also have been stripped or skimmed from the black liquor.

The chemicals in the cooking liquor are present in the black liquor as the inorganic fraction. A portion of the inorganic fraction is involved in reactions with the organic material dissolved in the black liquor during the cooking and another portion of the inorganics is involved in reactions after the cooking. Only the sulfur present as sulfide ion (S^{-2}), that can be converted to thiosulfate ion ($S_2O_3^{-2}$) in the brown stock washing or in an oxidation plant, is discussed here.

The pulp yield calculated after the cooking on a bone dry pulp basis can vary considerably for different processes, grades of pulp, and species of wood.

The majority of recovery boilers are used for burning kraft liquor. Some are used for bisulfite liquor or for cross-recovery for kraft and neutral sulfite pulping liquor. The characteristics of bisulfite and NSSC liquors can deviate considerably from the normal kraft liquors.

The dry solids content of the black liquor from the kraft pulping process can vary over a wide range. Some extreme values are shown in Table 10-1.

TABLE 10-1
BLACK LIQUOR DRY SOLIDS CONTENT

Process	Dry Solids Content*	
	kg/t	(lb/ton)
Linerboard pulp	1,100	(2,200)
Paper-grade pulp	1,000	(2,000)
Dissolving pulp	2,250	(4,500)

*Based on air-dried ton of production.

Changes in the reduction ratio (ratio of sulfide sulfur to total sulfur) and the causticizing efficiency (molar ratio of NaOH to NaOH plus Na_2CO_3) in the white liquor must be monitored since these changes influence the dry solids composition.

The heat value of the black liquor dry solids varies with the composition and is higher for black liquors of high lignin content. The amount of air needed for complete combustion is also higher for liquors of high lignin content. The heat value and the air required for complete combustion are related linearly. The deviations, however, from this linear relationship are, in many cases, of the same magnitude as the amount of excess air that can be used for combustion in a recovery boiler. The deviations from the linear relationship are increased by variations in the reduction, causticizing efficiency, and residual alkali in the black liquor. Figure 10-1 shows the bomb heat values (BHV) of softwood and hardwood lignins and an average pulp carbohydrate composition as functions of the oxygen required for complete combustion. Figure 10-2 shows the BHV for some North American black liquors and the maximum observed deviations from the indicated linear relationship.

The amount of air needed for the combustion and the amount of flue gas can easily be determined if the elemental analysis of the black liquor dry solids and the water content in the black liquor are known. The elemental analysis should represent the same stage in the process as the figure for the dry solids fired. One method of calculation of air and flue gas flows is shown in Appendix 10-1.

The BHV should be determined for the black liquor without drying it in advance. Investigations show that considerable changes take place in the heat value of the black liquor dry solids if it is dried to a powder before it is put in the bomb (3) (4). A black liquor sample of 60-70 percent solids is placed in the bomb and a small amount of paraffin oil is added on top to increase the heat generation, to get complete combustion without residual carbon in the ash, and to prevent the dry solids ash from splattering out of the sample holder. The air should not be purged from the bomb as the very small amounts of nitric oxides formed during combustion are useful as a catalyst for oxidizing all sulfur to sulfate. The heat value determined in this way has a much smaller variance than the heat value determined according to the method of drying the black liquor to a powder. By relating the BHV to the black liquor, the error introduced by the method of determining the black liquor to dry solids is bypassed. Comparisons of heat values before and after black liquor oxidation should be made using sodium as a reference element because of the change in dry solids concentration. Comparisons of heat values before and after a direct contact evaporator can be made by adding another reference element to the black liquor as sodium is packed up with ash in the flue gas.

The combustion products in the bomb are in the fully oxidized stage if made with the modified procedure. Two cases can be considered depending upon the molar ratio S/Na_2. This ratio is normally less than 0.4 for kraft liquor, but could be more than 1 for sodium bisulfite liquor. The combustion products are shown in Table 10-2.

The influence of the formation of carbonic acid (H_2CO_3) and the uneven distribution of H_2SO_4 in different condensate drops may be neglected.

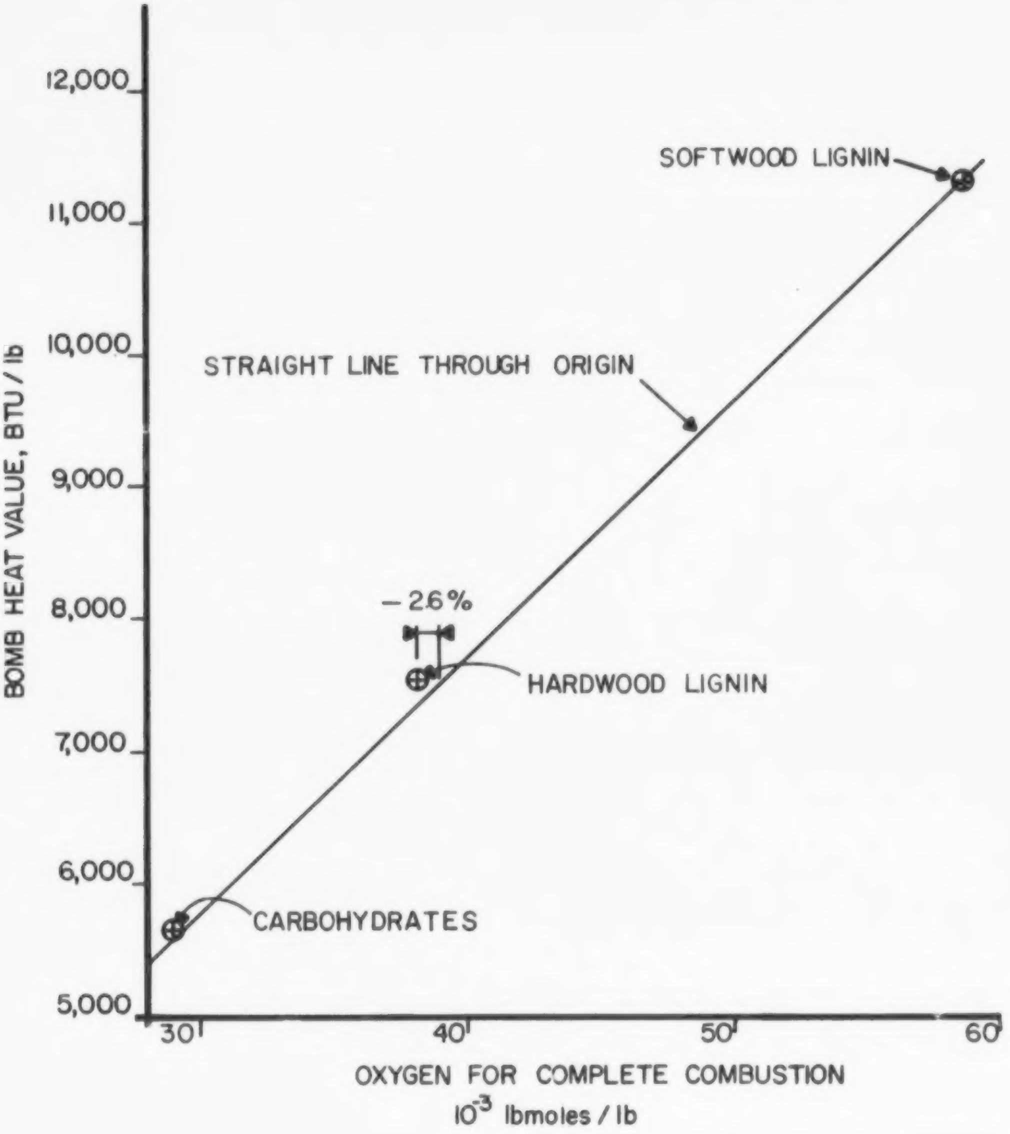


FIGURE 10-1

HEAT VALUES VS. OXYGEN DEMAND FOR COMPLETE COMBUSTION OF LIGNIN AND CARBOHYDRATES

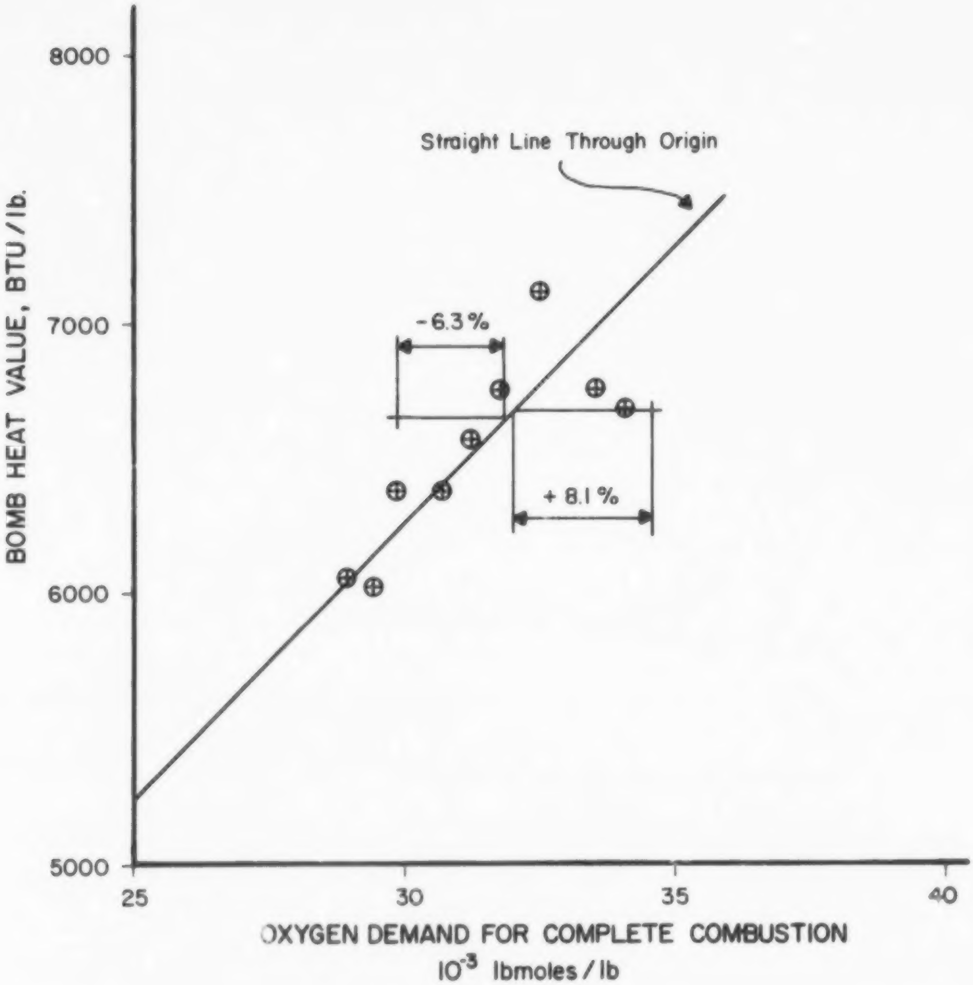


FIGURE 10-2

HEAT VALUES VS. OXYGEN DEMAND FOR COMPLETE COMBUSTION FOR SOME NORTH AMERICAN DRY SOLIDS

The combustion products from the components of the dry solids in the boiler differ from those of the bomb. For the different S/Na_2 ratios, the combustion products are shown in Table 10-3.

The compounds given in parentheses in Table 10-3 should be kept low in quantity for acceptable operating conditions. The flue gas might, during incomplete combustion, also contain H_2S, CO, H_2CH_4, and CH_3SH.

TABLE 10-2
BLACK LIQUOR COMBUSTION PRODUCTS IN CALORIC BOMB USING MODIFIED TECHNIQUE

	S/Na_2	
Phase	**Less than 1.0**	**Greater than 1.0**
As ash	Na_2SO_4, Na_2CO_3	Na_2SO_4
As gas	CO_2	CO_2
As condensate	H_2O, H_2CO_3	H_2O, H_2SO_4

TABLE 10-3
BLACK LIQUOR COMBUSTION PRODUCTS IN RECOVERY FURNACE

	S/Na_2	
Phase	**Less than 1.0**	**Greater than 1.0**
As smelt	Na_2S, Na_2CO_3 (Na_2SO_4, $Na_2S_2O_3$, Na_2S_n)	Na_2S, Na_2CO_3 (Na_2SO_4, $Na_2S_2O_3$, Na_2S_n)
As gas	CO_2, (SO_2), H_2O	CO_2, SO_2, H_2O
As dust entrained in the gas	Na_2SO_4, Na_2CO_3	Na_2SO_4, Na_2CO_3
As condensate	nil	nil

Chlorides in the dry solids will form sodium chloride in the smelt and the dust, as well as hydrogen chloride (HCl) and free chlorine (Cl_2) in the gas.

Corrections have to be made for the actual combustion products in the recovery boiler and applied to the calculations for the furnace design and steam generation.

The amount of flue gas and the release of heat can vary considerably, as calculated per ton of pulp. Furthermore, the ratio between flue gas and heat release does not have a constant value, but has to be considered during design of the recovery boiler to produce the correct temperature in the furnace and to produce the correct temperature of the superheated steam generated in the boiler. These facts complicate the design and operation of recovery boilers. The American method of stating the recovery boiler capacity in pounds of dry solids per day is less inexact than the old European method of rating in tons of pulp per day.

Turpentine and soap are formed during the cooking, especially in the pulping of softwood. The turpentine is released in the vapor form but the soap is dissolved in the liquor. Some of the soap is skimmed from the black liquor and used for the production of tall oil, which is a valuable byproduct. The remaining soap in the black liquor adversely affects the operation of the evaporation plant. The soap has a high heat value and will cause complications in the furnace if it is not efficiently removed.

10.1.2 Comparison of American and Scandinavian Liquor Concentration Methods.

The concentration of the black liquor from the brown stock washing depends on the equipment in the washing department. The black liquor concentration is increased with the number of theoretical exchange units in the brown stock washing and with higher losses of pulp, if such can be allowed. The black liquor concentration normally ranges between 15 and 18 percent dry solids. It is not possible to burn black liquor at this low concentration. It must be concentrated to at least 55 percent, and normally 60-65 percent dry solids, before injection into the recovery boiler. The dry solids concentration refers to the solids present when the black liquor leaves the evaporation unit and does not include the chemicals from the ash hoppers or dust collectors. The hopper and precipitator ash mixed with the black liquor increases the black liquor concentration by 3-4 percent.

The flow of the inorganic and organic compounds within a North American black liquor recovery boiler is shown in Figure 10-3. This figure assumes the use of a dry ash conveyor system for the boiler tube bank, the economizer, and the electrostatic precipitator. The normal practice in North America has been, however, to use the black liquor in the ash hoppers and the electrostatic precipitator to convey the ash back to the furnace. Figure 10-3 illustrates the change in the ratio between inorganic and organic contents of the black liquor within the recovery boiler department. It does not, however, show the changes in the composition of the black liquor that take place in the direct contact evaporator.

It is possible to use a fluidized bed incinerator for the combustion of black liquor, in which case a lower concentration, down to 35 percent, can be injected into the reactor. The chemicals are, however, not recovered in a suitable form for further processing, and the heat recovery as steam is much decreased. These facts make the use of fluidized bed apparatus for the recovery of kraft black liquor uneconomical except for very small plants. Figure 10-4 shows, in principle, the flow of the inorganic and organic contents through such a system.

The concentration of the black liquor before injection into the recovery boiler furnace can be effected in several ways. Most older recovery boilers in the United States and Canada use a multiple-effect evaporation plant to concentrate the brown stock wash liquor to about 50 percent. Direct contact evaporators are then used for concentrating up to about 65 percent solids before injection into the boilers. Three different types of direct contact evaporators have been used. These are cascade evaporators, cyclone evaporators, and venturi scrubbers. The flue gases are normally cooled from 400° C (750° F) to an exit temperature of 110 to 150° C (230 to 300° F).

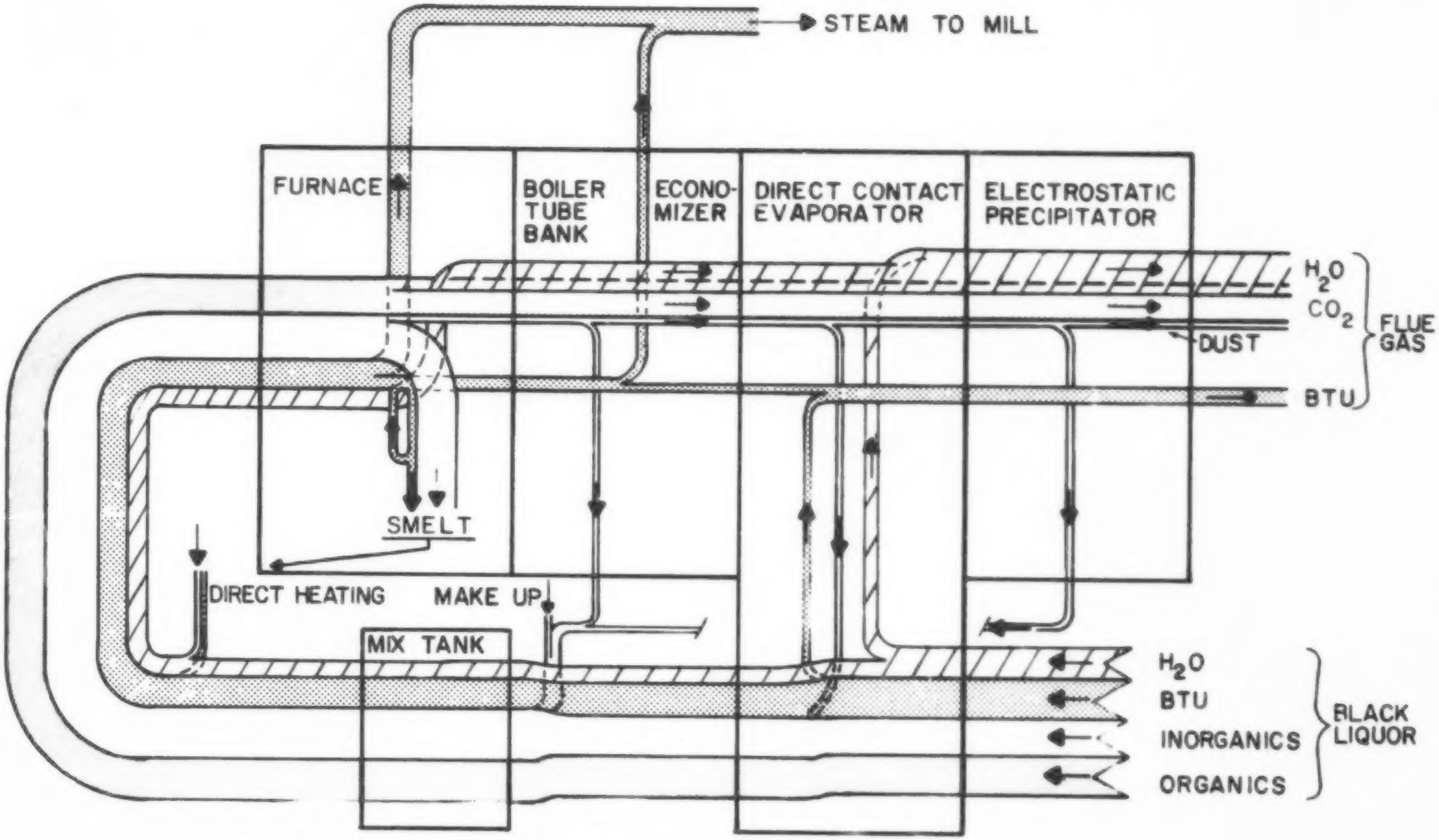

STEAM TO MILL
FURNACE
BOILER TUBE BANK
ECONO-MIZER
DIRECT CONTACT EVAPORATOR
ELECTROSTATIC PRECIPITATOR
H_2O
CO_2
FLUE GAS
DUST
BTU
SMELT
DIRECT HEATING
MAKE UP
MIX TANK
H_2O
BTU
INORGANICS
ORGANICS
BLACK LIQUOR

FIGURE 10-3

FLOW DIAGRAM FOR BLACK LIQUOR THROUGH RECOVERY BOILER-NORTH AMERICAN SYSTEM

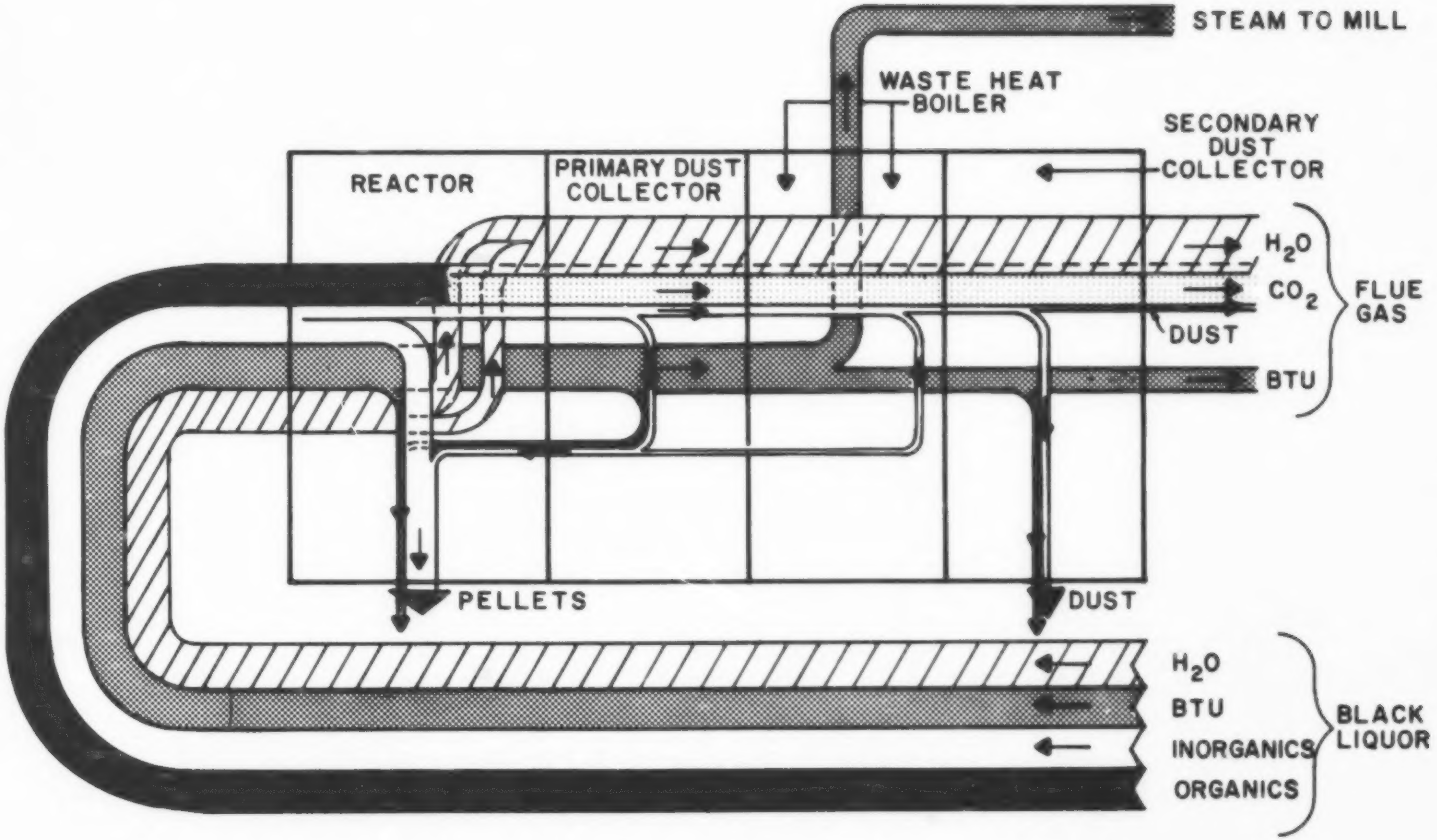

STEAM TO MILL
WASTE HEAT BOILER
SECONDARY DUST COLLECTOR
REACTOR
PRIMARY DUST COLLECTOR
H_2O
CO_2
DUST
BTU
FLUE GAS
PELLETS
DUST
H_2O
BTU
INORGANICS
ORGANICS
BLACK LIQUOR

FIGURE 10-4

FLOW DIAGRAM FOR BLACK LIQUOR THROUGH FLUIDIZED BED REACTOR WITH WASTE HEAT RECOVERY BOILER

The use of multiple-effect evaporation alone to achieve 60-65 percent concentration has been practiced at all pulp mills in Sweden and about half of the pulp mills in Finland. The concentration of the black liquor at furnace injection has been increased from about 50 percent in 1940 to 60-65 percent today. Figure 10-5 illustrates the flow of the inorganic and organic contents through such a system.

The two different approaches to the evaporation of the black liquor both have their advantages. The Scandinavian method of concentrating the black liquor exclusively by multiple-effect evaporators for injection into the boiler will give greater steam generation. The American method of employing recovery boilers with direct contact evaporators are less expensive to install. They are also self-compensating for capacity at overloading of the recovery boilers. The exit temperature of flue gas at the direct contact evaporator will increase at increasing load. This increase means that more heat is available for the final concentration of the black liquor. The additional heat is normally sufficient to compensate for the attendant lower dry solids concentration from the multiple-effect evaporator, which also is a result of overloading.

Overloading a Scandinavian-type recovery boiler normally means that the black liquor from the evaporation plant will have a lower solids concentration; however, the overall heat transfer coefficients will increase at lower concentrations, and the influence of the boiling point rise on heat requirements will, therefore, be reduced. This reduction will limit the decrease in concentration to some extent. The steam-generation rates of the Scandinavian system and of the American system would be approximately the same if the dry solids concentration after evaporation are the same. Furthermore, the flue gas flow in the furnace would be higher with the Scandinavian system since the final concentration of the black liquor is made in the furnace. This fact tends to increase the vertical velocity of the flue gas and to increase carryover of dry particles from the black liquor and their subsequent combustion in suspension. The emission of H_2S in the flue gases is lower than with direct contact evaporators operating with no oxidation of the black liquor, even under the adverse conditions of overloaded boilers. There may also be a certain decomposition of the dry solids in the direct contact evaporators, which will decrease the steam generation rate. Investigations, however, of the decomposition reactions taking place in the direct contact evaporators are not conclusive. Decreases in heat value of the dry solids by as much as 6 percent have been reported (5).

The lower capital cost for the American system and the possibility of increasing the load on the recovery boilers while maintaining combustion conditions as allowed by the self-compensating characteristics of the direct contact evaporators were very attractive to the Scandinavian pulp engineers. Investigations were made on the economics of the American and Scandinavian recovery boiler designs and operation. The feasibility of the Scandinavian design was investigated, and the additional investment was, in most cases, found attractive because of higher energy efficiencies. The fuel and power prices in Scandinavia, however,

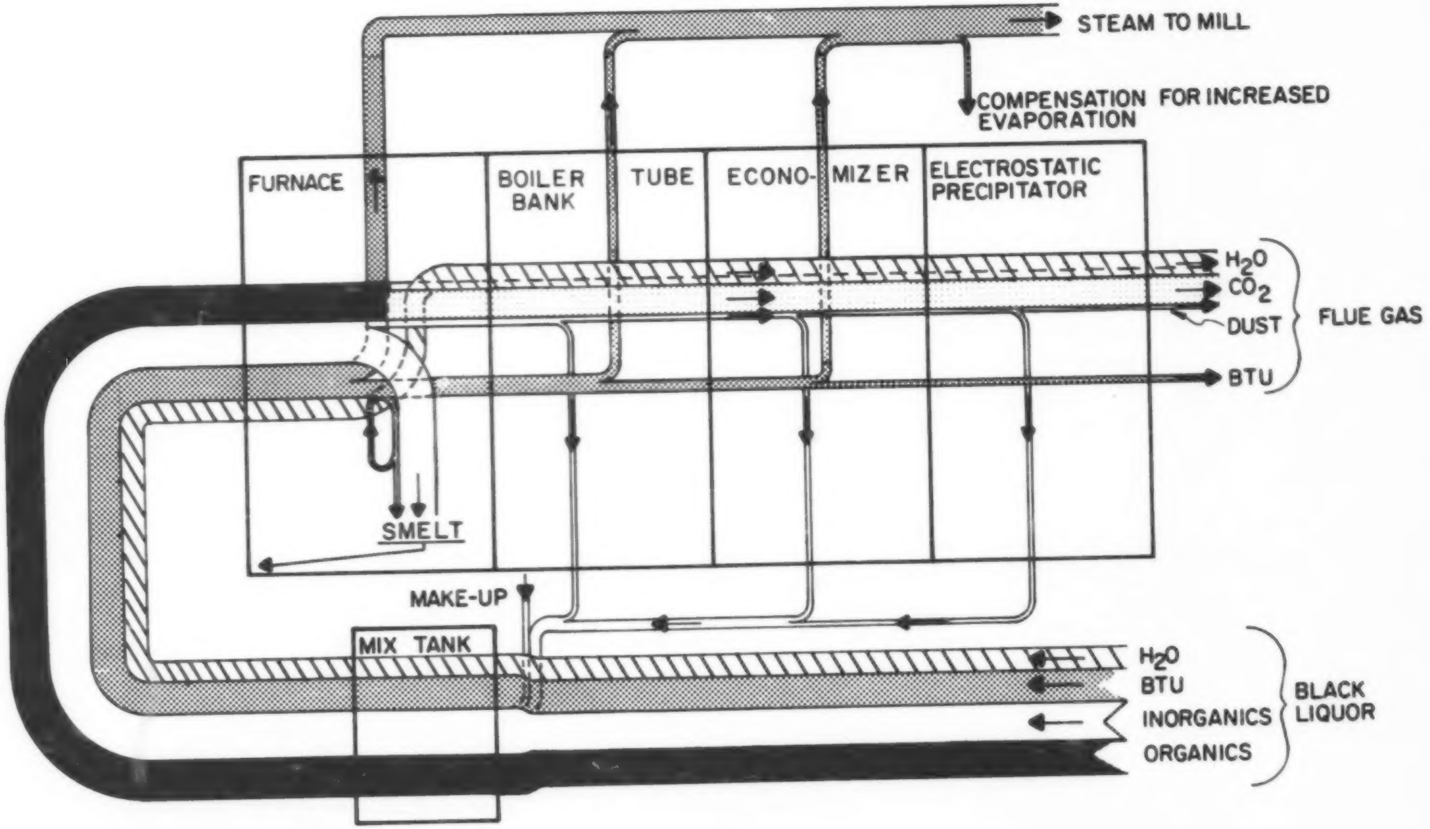

STEAM TO MILL
COMPENSATION FOR INCREASED EVAPORATION
FURNACE
BOILER BANK
TUBE
ECONO-MIZER
ELECTROSTATIC PRECIPITATOR
H_2O
CO_2
DUST
BTU
FLUE GAS
SMELT
MAKE-UP
MIX TANK
H_2O
BTU
INORGANICS
ORGANICS
BLACK LIQUOR

FIGURE 10-5

FLOW DIAGRAM FOR BLACK LIQUOR THROUGH RECOVERY BOILER
SCANDINAVIAN SYSTEM–LOW ODOR SYSTEM

were considerably higher than in most parts of the United States and Canada. An updated comparison of the conditions on the marginal investments is given in Tables 10-4, 10-5, and 10-6.

The flue gas from an American recovery boiler with a direct contact evaporator has a higher water vapor content than the flue gas from a Scandinavian recovery boiler with a large economizer. The higher moisture condition is very advantageous for the operation of the electrostatic precipitators traditionally used for collection of dust from flue gas. A higher voltage can be used with higher water vapor content, and the handling characteristics of the dust are better at a lower temperature and a higher water content. (The favorable tendency of cooling has a practical limit at about 115° C (240° F), and the dust absorbs so much

TABLE 10-4
OPERATING CONDITIONS FOR AMERICAN AND SCANDINAVIAN BLACK LIQUOR CONCENTRATION*

Assumed Operating Conditions	American Practice	Scandinavian Practice
Dry solids, kg/hr (lb/hr)	45,000 (100,000)	45,000 (100,000)
Fuel heat value, cents/million Btu	85	85
Steam heat value, cents/million Btu	95	95
Cost of electric power, cents	120/kW month +0.6/kWh	120/kW month +0.6/kWh
Heat consumption by back pressure power generation, Btu/kWh	4,000	4,000
Black liquor concentration at:		
Washers, %	17	17
Evaporators, %	50	63
Direct evaporators, %	63	–
Furnace	63	63
Heat consumption in s-effect evaporation, Btu/lb	235	235
Exit flue gas temperature, °C (°F)	150 (300)	150 (300)
Flue gas CO_2 content afterboiler, %	18	18
Marginal investment costs for:		
Back pressure turbine, $/kW	–	60
Power boiler (steam generating section alteration included), $/lb steam	6	6

*Oil and power prices and investment costs based on data available in Sweden, September, 1973.

TABLE 10-5
CAPITAL COST COMPARISON OF AMERICAN AND SCANDINAVIAN BLACK LIQUOR CONCENTRATION PRACTICES

Item	American Practice $	Scandinavian Practice $
Direct contact evaporator	200,000	–
Larger evaporator plant	–	600,000
Larger recovery boiler	–	600,000
Larger back pressure turbine	–	30,000
Larger power boiler	150,000	–
Total	350,000	1,230,000
Difference in capital cost	880,000	

TABLE 10-6
ANNUAL OPERATING COST COMPARISON OF AMERICAN AND SCANDINAVIAN BLACK LIQUOR CONCENTRATION PRACTICES

	Conversion from North American to Scandinavian Practice	
Item	Increases $	Decreases $
Cost of evaporation	73,300	–
Evaporator maintenance	6,000	–
Recovery boiler steam value	–	324,900
Recovery boiler maintenance	8,000	–
Power generation value	–	15,800
Turbine maintenance	600	–
Maintenance of power boiler	–	3,000
Total	87,900	343,700
Total decrease in annual operating cost	255,800	

Gross margin: $\frac{255,800}{880,000} \times 100\% = 29\%$

humidity from the gas that handling the dust becomes extremely difficult.) Higher migration velocities could, therefore, be observed in the precipitators operating after the direct contact evaporator than those after a recovery boiler using a large economizer for cooling flue gas and using the black liquor which was fully concentrated in the multiple-effect evaporators. The characteristics of different types of direct contact evaporators are discussed in section 10.3, Boiler Design, and in more detail in section 10.6, Direct Contact Evaporation.

10.2 Combustion of Black Liquor Dry Solids

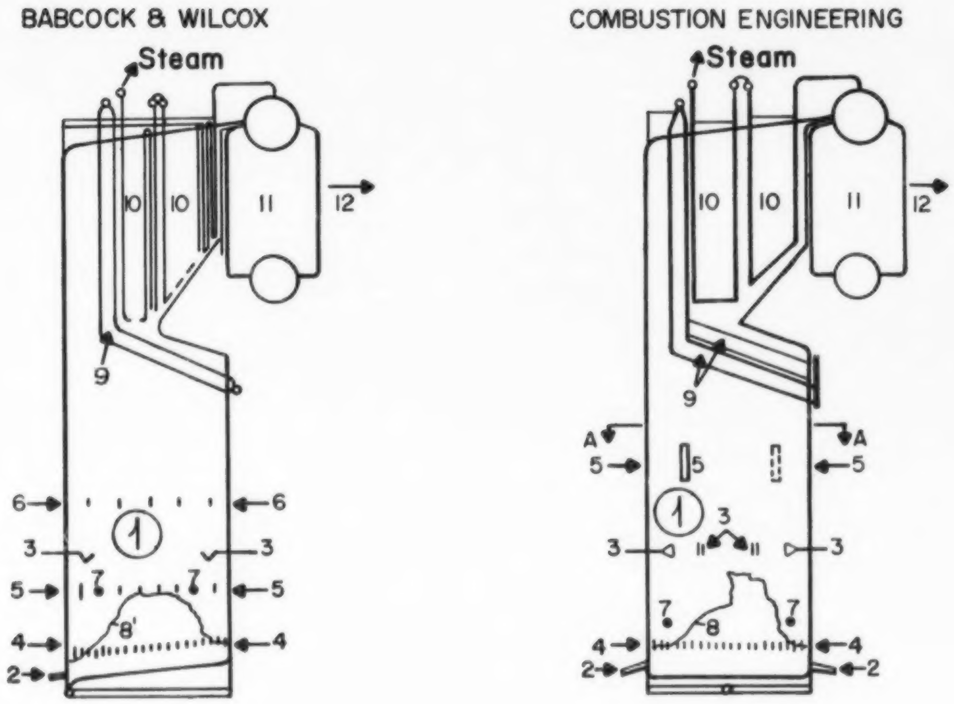
10.2.1 Arrangement of Combustion

The two main objectives in operating a recovery boiler are to recover the chemicals in the reduced state (that is, the sulfur should be present as sulfide and not sulfate) and to recover the heat to generate steam for the process. The value of the chemicals has normally been much higher than the value of the heat in the dry solids. It has, therefore, been standard practice when fuel has been inexpensive to reduce the cost of the very expensive recovery boiler installation by accepting a low heat recovery and producing the necessary steam in a separate power boiler.

The combustion within a recovery boiler has to be separated into two zones because of the two different objectives of the recovery boiler operation. The first zone has to be maintained under reducing conditions less than the stoichiometric amount of air. The products of this zone are a discharge of the chemicals in the molten state with the sulfur present mainly as sulfide and a discharge of the organic matter as a gas having considerable heat value. The second zone of the combustion starts with the addition of secondary air. The amount of secondary air corresponds to the amount of additional air theoretically needed for complete combustion of the gas, plus an excess of about 10 to 20 percent.

Figure 10-6 is a schematic drawing of two recovery boiler furnaces. The left hand figure is the Babcock & Wilcox (B&W) design. The nozzles for the primary air (item 4 in the figure) and the secondary air (item 5 in the figure) are shown. The right-hand figure shows the primary and secondary air supply, according to another manufacturer, Combustion Engineering (CE). In the Babcock & Wilcox (B&W) design, some of the secondary air is introduced at a higher level (item 6 in the figure) and is normally referred to as tertiary air.

The black liquor is sprayed in rather small drops over the cross section of the furnace through the flue gases. The intention is to dry the black liquor droplets to a concentration where the heat value of the char material with the residual moisture is sufficient to keep a reasonably stable combustion going. The liquor spray nozzles can be placed as item 3 in Figure 10-6 indicates. The black liquor dry solids are collected in the bottom of the


BABCOCK & WILCOX
Steam
10
10
11
12
9
6
1
3
5
7
8'
4
2
COMBUSTION ENGINEERING
Steam
10
10
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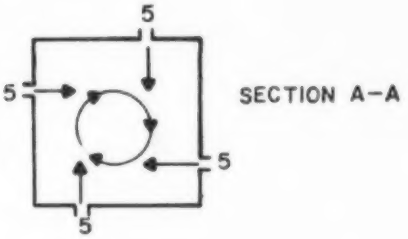


SECTION A–A

LEGEND

1. Furnace
2. Smelt Spouts
3. Black Liquor Spray Nozzles
4. Primary Air Supply
5. Secondary Air Supply
6. Tertiary Air Supply
7. Position of Char Bed Burners for Oil or Gas
8. Normal Configuration of Char Bed
8'. Same at Low Primary Air Flow and Pressure
9. Screen Tubes
10. Superheater
11. Boiler Tube Bank
12. Exit to Economizer

FIGURE 10-6

PRINCIPLE DESIGN OF AIR DISTRIBUTION TO RECOVERY BOILER FURNACES recovery boiler furnace in a char bed. The air burns off the dry solids from the top of the char bed, which normally has the form indicated in the left-hand part of Figure 10-6.

The primary air is supplied around the circumference of the recovery boiler furnace. The air supply should be distributed with a fairly constant ratio to the local supply of black liquor dry solids. The primary air is normally preheated to a temperature of 150° C (300° F). Some boilers with higher primary air temperatures have been made. The primary air jets will penetrate a certain distance into the furnace depending on the size of the jets and their velocity. The oxygen in the air will be consumed in the combustion during the penetration of the jet into the furnace. The partial pressure of the oxygen in the border zone between the flue gas atmosphere and the char bed will, therefore, vary over the whole extension of the air jet. The temperature will also vary. The oxygen partial pressure and the temperature are the two main parameters that determine the combustion conditions in a limited spot. The combustion conditions and the equilibrium conditions will, therefore, vary over the entire cross section of the furnace. One Scandinavian manufacturer (Götaverken) introduces some of the primary air at a higher level and with a wider spacing between the nozzles and at a considerably higher pressure than for the conventional primary air supply. This is called high primary air and the arrangement is shown in the left-hand part of Figure 10-7. The conventional design is shown in the right-hand part of the figure. The char bed will form as indicated in the figure. Other Scandinavian manufacturers are using secondary air for the same purpose as high primary air (6).

The flue gases formed during primary and secondary air combustion cool by radiation to the furnace walls to about 870° C (1600° F) before they enter the convection heating surfaces (i.e., the screen tubes, the superheater, and the tube boiler bank). The flue gas has a temperature of about 450° C (850° F) after the tube boiler bank. The flue gases are then further cooled in an economizer to about 400° C (750° F) in the American system with the direct contact evaporator and to about 160° C (320° F) in the Scandinavian system. Two typical American recovery boilers of modern design with economizers instead of direct contact evaporators are shown in Figures 10-8 and 10-9 for B&W and for CE, respectively.

The reason for having a recovery boiler furnace large enough to allow the flue gases to cool to about 870° C (1600° F) before they enter the convection surfaces is to allow complete combustion of entrained organic particles before they can reach the coder tube surfaces. The deposits from organic matter have been shown to be much more difficult to remove from the heating surfaces than normal tube deposits.

Burners for oil or natural gas to supply heat to the lower part of the furnace are arranged as indicated in Figure 10-6, item 7. These burners are used to:

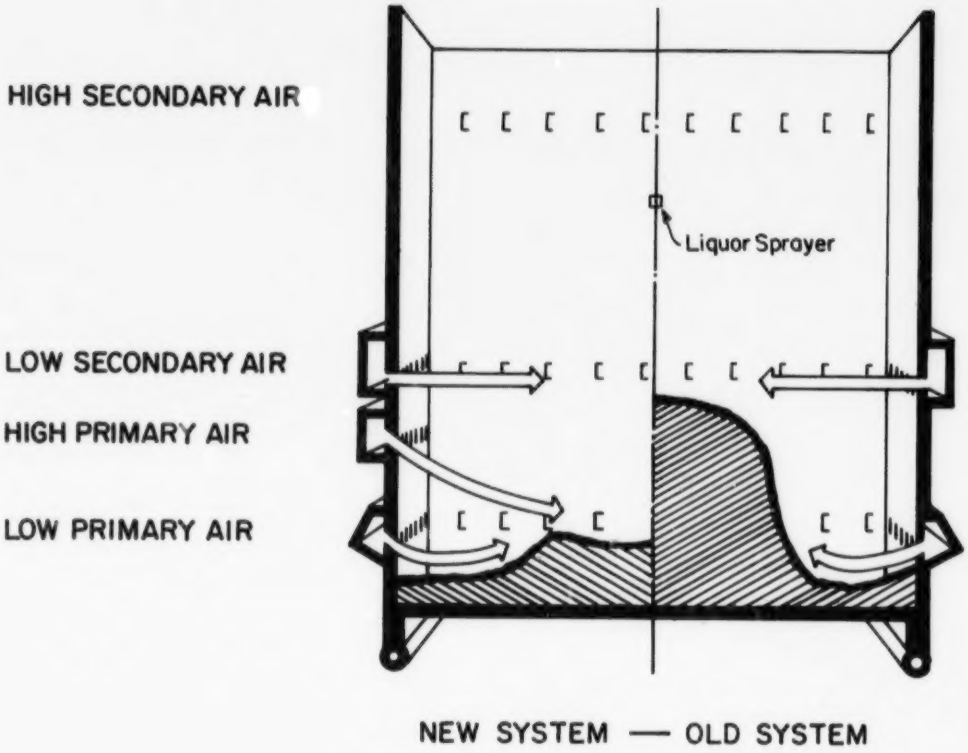

HIGH SECONDARY AIR
Liquor Sprayer
LOW SECONDARY AIR
HIGH PRIMARY AIR
LOW PRIMARY AIR
NEW SYSTEM — OLD SYSTEM

FIGURE 10-7

AIR SUPPLY ACCORDING TO GÖTAVERKEN ÅNGTEKNIK AB DESIGN

1. Bring the recovery boiler up to operating temperature and to supply heat for drying the injected black liquor drops.

2. Supply additional heat to increase the temperature in the furnace to stabilize the combustion during disturbances.

3. Smelt down the bed at shutdowns to allow inspection of the lower part of the walls and the bottom of the furnace, and

4. Supply heat for additional process steam generation when the black-liquor supply is not sufficient.

The first three uses of the burner are necessary for the operation of the boiler. The fourth use is only justified when operating the recovery boiler so that enough heat is supplied for process steam generation. It coincides in this case with the second use mentioned. Steam in excess of the normal rating should be generated by load carrying oil or gas burners placed at

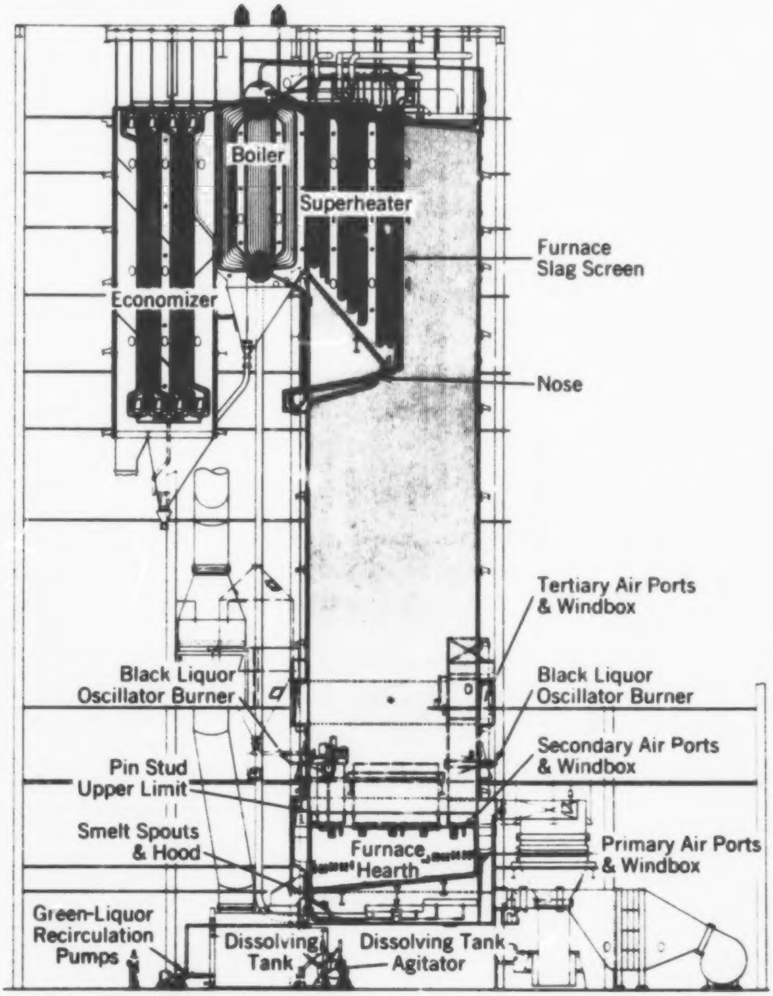
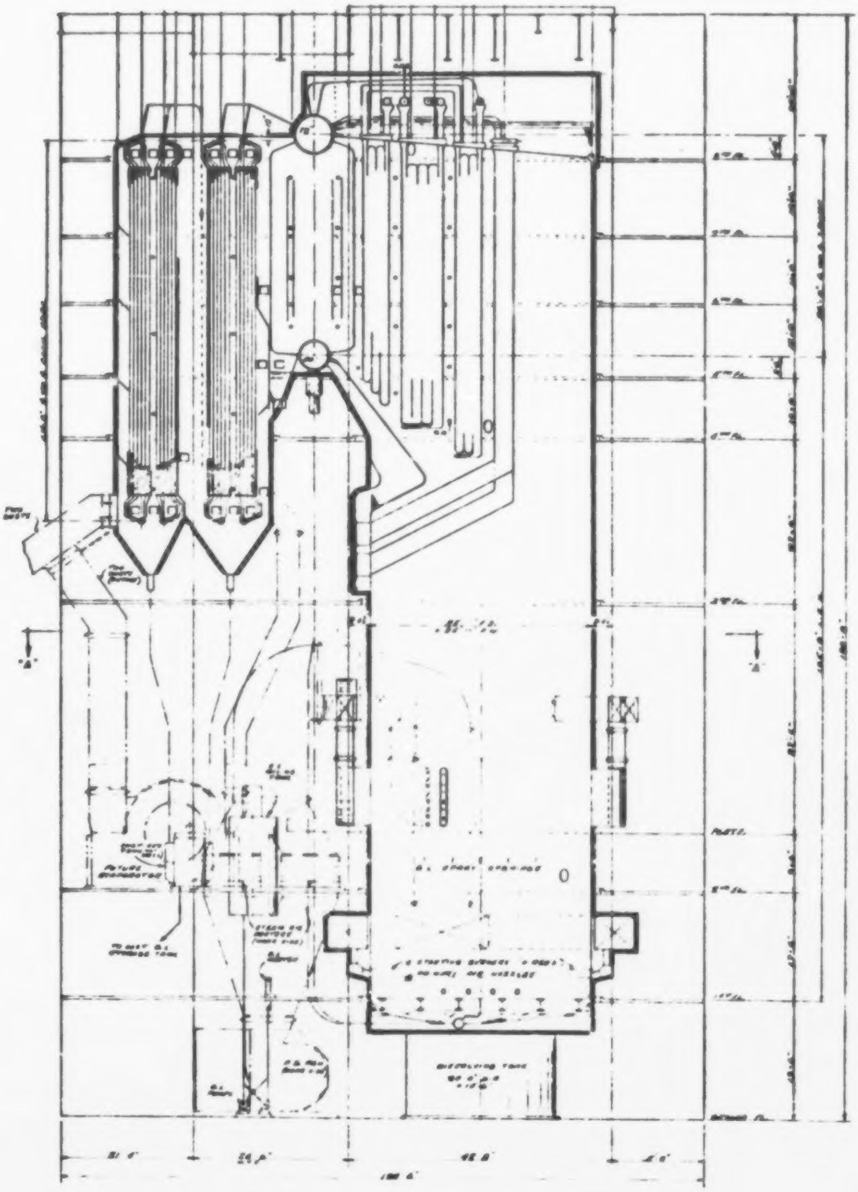

Boiler
Superheater
Furnace Slag Screen
Economizer
Nose
Tertiary Air Ports & Windbox
Black Liquor Oscillator Burner
Black Liquor Oscillator Burner
Secondary Air Ports & Windbox
Pin Stud Upper Limit
Smelt Spouts & Hood
Furnace Hearth
Primary Air Ports & Windbox
Green-Liquor Recirculation Pumps
Dissolving Tank
Dissolving Tank Agitator

FIGURE 10-8

MODERN KRAFT RECOVERY UNIT FROM BABCOCK & WILCOX

a higher level in the recovery boiler. This position will also tend to keep the temperature of the superheated steam at the correct value since the ratio of flue gas flow to steam generation is considerably lower for oil and gas than for black liquor.

The operation of auxiliary fuels in the recovery boiler presents an explosion hazard. Detailed instructions about the installation and operation of such burners have been made by the Black Liquor Recovery Boiler Advisory Committee (BLRBAC) (7) (8). Instructions about emergency shutdown procedures are also given by BLRBAC.



SECTIONAL SIDE ELEVATION

FIGURE 10-9

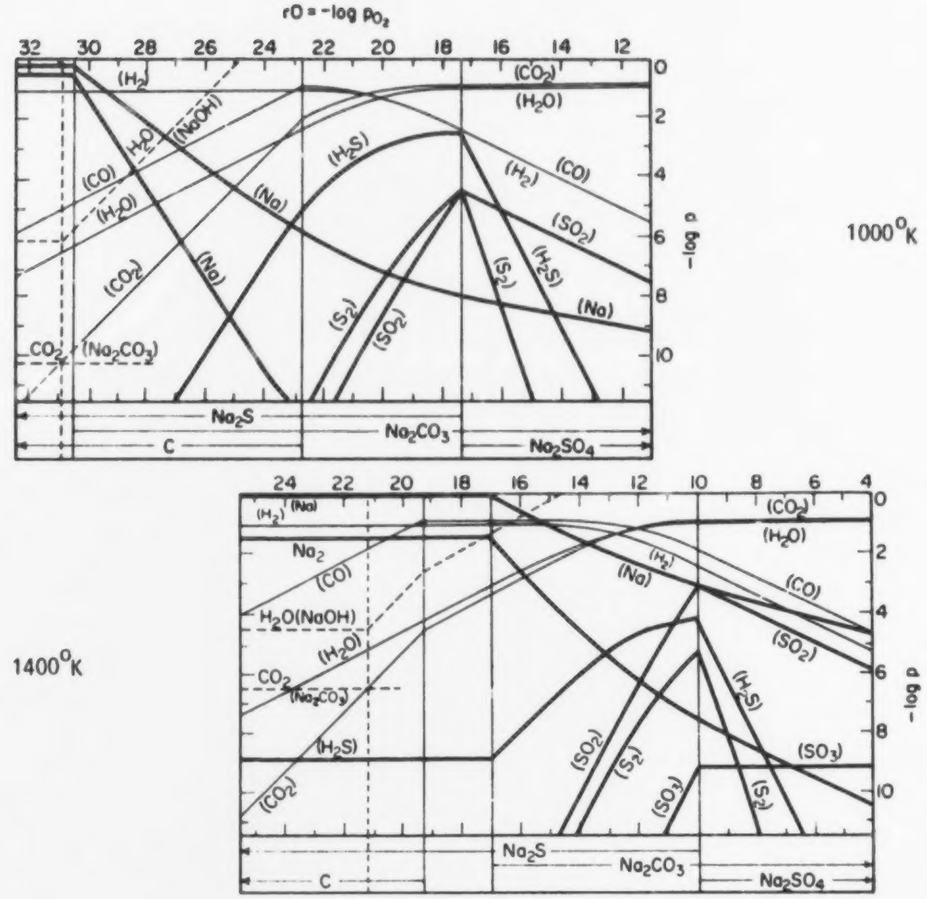
MODERN KRAFT RECOVERY UNIT FROM COMBUSTION ENGINEERING

10.2.2 Reactions in the Primary Air Zone

A standard for operating the recovery boiler to obtain the proper reactions from the process was developed by observing the effects of disturbances in the combustion process and of changes in operation parameters.

A typical example illustrating this state of knowledge is as follows: The combustion in the hearth could, at local spots, have an insufficient rate of combustion and a low temperature, resulting in a condition sometimes called "black out." The remedy was to use a compressed air lance to blow the black char from the wall and reignite the local spot. Heavy corrosion was often observed at places where black out conditions were common. Air lancing was believed to be the reason for this corrosion. Compressed air lances were also used at places with normal combustion without any resulting corrosion. It was then deduced that the black out conditions themselves were responsible for the corrosion, but the mechanism was not understood. Many of the problems that arise in attempting to achieve stable combustion without forming local black out conditions are caused by the necessity of reaching a compromise between two competing design requirements in providing sufficient reaction surface between fuel and primary air. The furnace cross section should have a relatively small size with the present arrangement to allow suitably high temperatures in the primary combustion zone. At the same time the cross section of the furnace has to exceed a minimum size to avoid high vertical gas velocity. A high vertical velocity would tend to entrain burning char pieces and black liquor drops. This carryover would result in buildup of deposits on the heating surfaces in the boiler following the furnace, and a higher dust load in the gas.

The very complicated combustion conditions for sodium-based pulping liquors have been investigated by Bauer and Dorland (9) by means of thermodynamic calculations of the equilibrium conditions at different temperature levels for a certain composition of black liquor. Bauer and Dorland used the negative logarithm of the partial pressure of oxygen ($rO = -\log_{10} O_2$) as the independent variable and negative logarithms of the partial pressures of the possible compounds ($-\log_{10} P$) in the flue gas as the dependent variable in determining equilibrium conditions. This method was introduced by Sillen and Andersson (10) for calcium bisulfite and magnesium bisulfite liquor. The possibility of complete emission of sodium or sulfur or both to the flue gas under certain furnace conditions and black liquor compositions exists (see Figure 10-10). The upper portion of Figure 10-10 shows an equilibrium diagram for condensed phases and partial pressures of gases for 727° C (1,340° F), and the lower portion shows the same diagram for 1,127° C (2,061° F). The kinetics of the possible reactions that can occur were not taken into account in preparing these diagrams. Rosen has extended the black liquor equilibrium studies to include variations in the black liquor water content and in the pressure (11).



Upper Diagram - NaOH and Na_2O cannot exist at this or higher temperatures.

Lower Diagram - The partial pressure of metallic sodium (Na and Na_2) is becoming more and more important as the temperature increases, and will lead to high fly ash losses.

FIGURE 10-10

EQUILIBRIUM DIAGRAM FOR CONDENSED PHASES AND GASES FOR A SODIUM BASED BLACK LIQUOR (9)

The previously cited work and other observations indicate that the release of sodium from the burning char of black liquor is mainly a function of the temperature and the gas conditions in the border zone between the bed and the flue gas. The total sulfur concentration and the sodium/sulfur ratio control the sulfur release to the flue gas. Figure 10-11 shows the conditions for a normal kraft liquor. Sodium is used to represent the base in the process. Small amounts of potassium are normally present in the wood and also in the makeup chemicals. Some potassium will, therefore, be present in the black liquor, but it will react in the same way as sodium. It has a lower boiler point and its compounds have a lower melting point. The influence of the potassium can normally be neglected except for mass balances.

The amount of sodium which is distributed to the flue gas increases sharply with the temperature, following a curve similar to a vapor pressure curve. The release of sodium is also influenced by the primary air velocity, which determines the diffusion conditions. The amount of sodium in the flue gas will increase considerably with increasing air velocity, and this relationship seems to indicate that the release of sodium could be by evaporation. The rate of evaporation would depend on the diffusion conditions in the border zone between the flue gas atmosphere and the bed. The sodium to sulfur ratio in the smelt is strongly dependent on the temperature. The release of sulfur to the flue gas will, therefore, be a function of the temperature, the Na_2/S ratio in the black liquor, and, possibly, of the absolute sulfur content in the black liquor.

Large variations in the Na_2/S ratio in the smelt have been observed during firing of bisulfite liquor of constant Na_2/S ratio. Variations in the smelt sulfidity have been observed to a lesser extent when firing kraft black liquor. The curves for sodium and sulfur release shown in Figure 10-11 are made for normal contents of sodium and sulfur, that is, 18 percent and 3.5 percent, respectively. At very low temperatures, 700° C (1,300° F), all the sulfur in the black liquor is released to the flue gas. This actually takes place at the shock pyrolysis as shown in the research for the Billerud-SCA process. Release of sulfur to the flue gas atmosphere decreases at increasing temperatures, but eventually increases again until total release occurs above 1,540° C (2,800° F). There should, consequently, be combustion conditions with a sufficiently high temperature and velocity to evaporate enough sodium to combine with all the sulfur released to the flue gas, provided that the molar S/Na_2 ratio is less than 1.0 in the dry solids.

The sulfur may be present in the flue gas over the bed as S, H_2S or SO_2. A low temperature favors the presence of S and H_2S. Elemental sulfur can also be formed by the combustion of H_2S with O_2 depending on the temperature and molar ratio. Elemental sulfur in the nascent state seems to be responsible for much of the observed corrosion on recovery boiler tubes (12) (13). Observations and analyses made in the last few years show a good correlation between the factors that influence the temperature in the furnace and the release of H_2S and SO_2 (14).

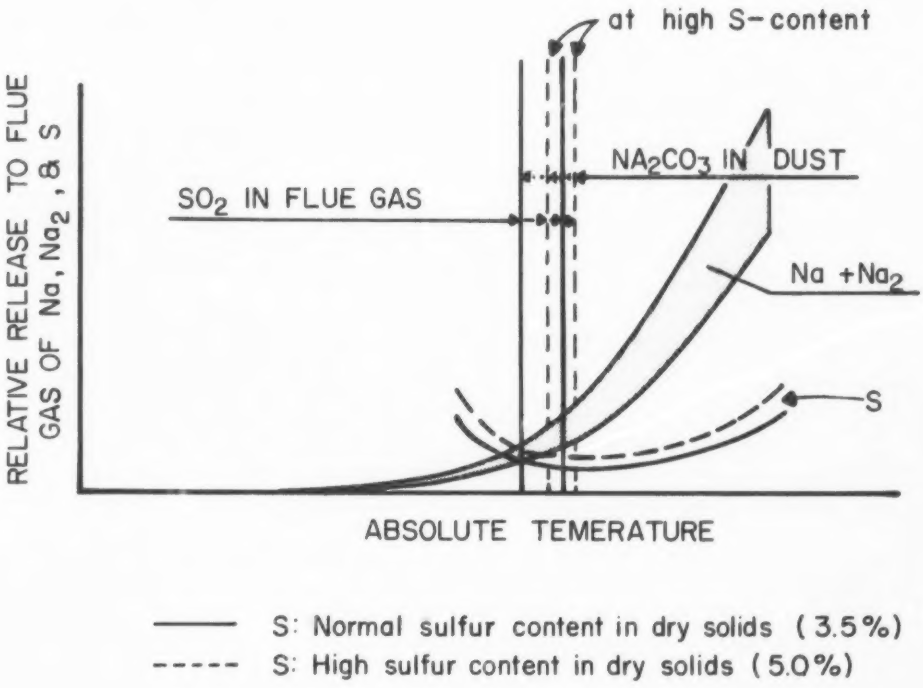


FIGURE 10-11

DISTRIBUTION OF SODIUM AND SULFUR IN A BLACK LIQUOR RECOVERY FURNACE AS A FUNCTION OF TEMPERATURE

H_2S is probably present in the flue gas in the primary air combustion zone at about 50 to 200 ppm if the temperatures in the border zone between the bed and the flue gas atmosphere are optimal for the operation. H_2S concentrations up to 15,000 ppm have been observed in this region when black out conditions were present. Small amounts of CH_3SH have been found in the primary air combustion zone, but no measurable amounts (<1 ppm) have been found at the entrance to the screen tubes when there was sufficient secondary air supply.

The sodium probably evaporates from the bed as elemental sodium and reacts with oxygen to form Na_2O within a very short distance from the bed. The Na_2O reacts with CO_2 to form Na_2CO_3 at the high temperature in the furnace. Part of the sodium compounds sublime to dust from the vapor phase. The black liquor droplets and agglomerates will pass through the primary air combustion zone. The volatile compounds will be partially stripped from the black liquor during the drying. Decomposition of the black liquor dry solids and pyrolysis and possibly combustion of the smallest fraction of the drops will start before the drops have reached the bed. The small amounts of mercaptans, organic sulfides, and hydrocarbons that are found may be stripped during the drying or the beginning of pyrolysis and are not necessarily products of the combustion itself.

Black liquor drops too small to fall downward can be carried upward by the flue gas and burn in the secondary air combustion zones. The temperature in the reaction zone can then reach much higher values than at normal combustion, and a higher than normal release of sulfur can take place.

The smelt is collected at the bottom of the bed and discharged through the smelt spouts to the dissolving tank. The melting point depends on the smelt composition (see Figure 10-12). The melting point increases considerably with contamination of calcium and decreases with the presence of potassium and chlorides (Figure 10-13). The melting point and the heat transmission rate determine the thickness of the smelt layer on the tubes.

10.2.3 Secondary Air Combustion

The final combustion starts immediately after the introduction of secondary air. The total amount of primary and secondary air must for most boilers be more than 110 percent of the theoretical air (that is, stoichiometric air). It should, on the other hand, be less than 125 percent to avoid the possible formation of sticky dust, which has a great tendency to foul the heating surfaces in the economizer and/or the collecting plates in the electrostatic precipitator. The two air limits correspond to 2 and 5 percent excess O_2 in the flue gas for an average kraft liquor.

By definition, the secondary air is the difference between the total air and the primary air. Some investigations indicate that the primary air flow should be between 60 and 70 percent of the theoretical air. The remaining air to be used as secondary air would be as a minimum 40 percent, and, as a maximum, 65 percent of the theoretical air. The secondary air should be supplied in the furnace so that it mixes with the gas coming from the primary air combustion zone below. The primary air combustion zone gas may have wide variations in its demand for oxygen to complete the combustion, depending on local variations in the bed. It is fortunate that it has been possible to achieve practically complete combustion in the recovery boilers without using very large amounts of excess air.

The secondary air is supplied according to two different methods by the main North American manufacturers of recovery boilers, as shown in Figure 10-6. The (low) secondary air is, in the B&W boilers, placed only a few feet above the primary air nozzles, and it controls, in many cases, the height of the bed in the center of the furnace. This air supply has, therefore, a mixed function, and acts along the walls as secondary air to complete the combustion of the gas, but in the center of the furnace as primary air to burn off the bed. The sum of the primary air and (low) secondary air is normally not sufficient to give complete combustion. The tertiary air in B&W boilers is supplied above the spray nozzles to

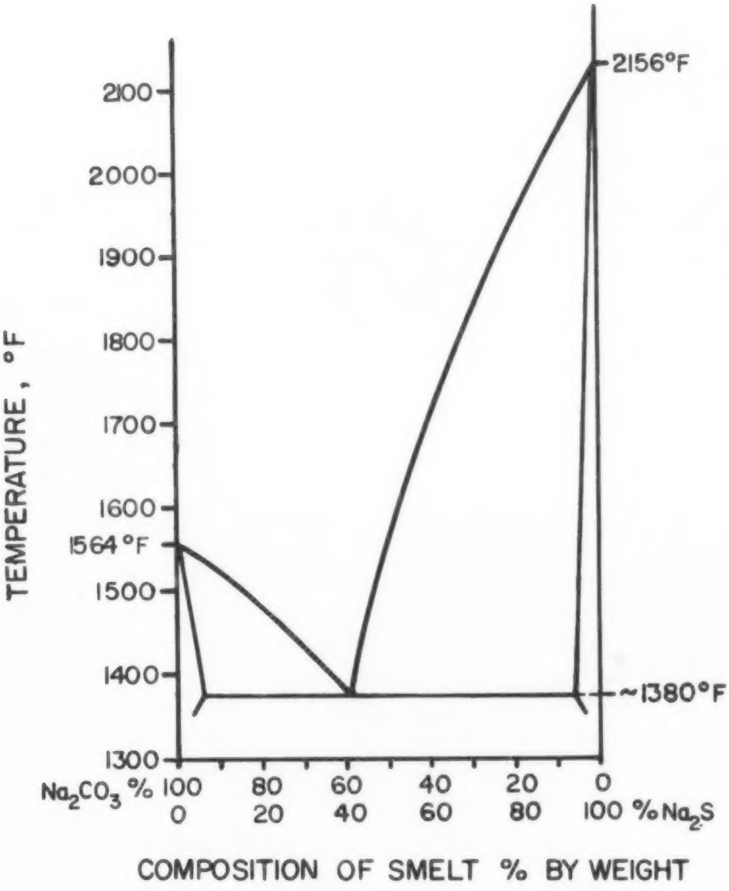


FIGURE 10-12

EQUILIBRIUM DIAGRAM FOR A Na_2CO_3-Na_2S SYSTEM (15)

give a reasonable amount of excess air to complete the combustion. The nozzles for the air cannot be controlled, and the velocity of the air is, therefore, proportional to the flow and to the absolute temperature of the air. This means that changes in the load or in the distribution will influence the velocity of the different air jets and the resulting turbulence which is presumed necessary for complete combustion.

The design of CE boilers according to Figure 10-6 uses a tangential air supply to produce a rotary movement of the gas in the furnace. Only four big nozzles are used, one in each wall. Each nozzle is divided into compartments which can be shut off individually to control the velocity in the air jet when the flow is changed. The tangential air supply was previously placed high in the furnace and the rotary movement tended to load one side of the superheater and boiler tube bank more than the opposite side. The air nozzles have recently been moved downwards in the furnace. This change should increase the temperature in the

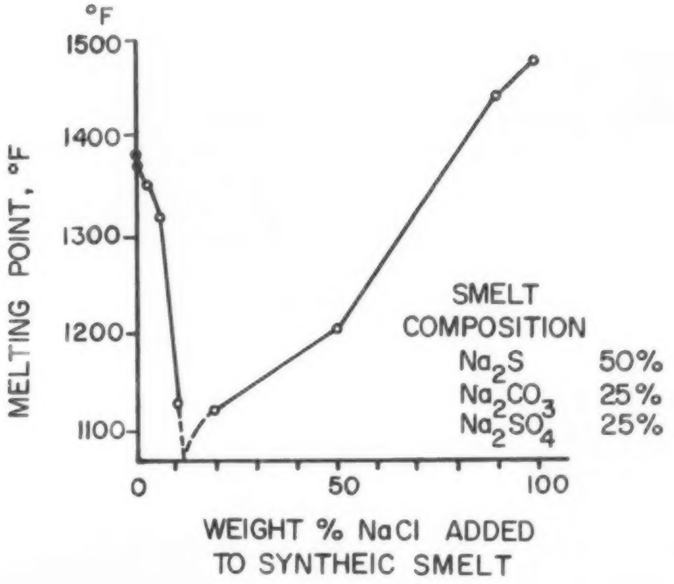


FIGURE 10-13

EFFECT OF NaCl ADDITION ON THE MELTING POINT OF A SYNTHETIC PULP

primary air combustion zone slightly, by radiation, and decrease the sideways influence on the furnace temperature distribution.

The design of a typical Scandinavian recovery boiler, such as shown in Figure 10-7, has the secondary air supply split between two levels. The low secondary air is placed above the primary air nozzles but below the spray nozzles, and on all four walls of the furnace. Most of the secondary is normally supplied at this level. The rest of the secondary air is supplied in the upper level of boilers as high secondary air or tertiary air. The high secondary air is supplied on two or four boiler walls.

All air nozzles are adjustable in the modern Scandinavian design. This feature allows control of the air velocity with total independence of the flow and allows distribution of the air between different levels. It also allows adjustment of the air distribution in response to the liquor spray pattern. This has proved very valuable, especially in cases where the boiler load was low during the start-up period of mill operation.

10.2.4 Formation of Particulate Matter

The flue gas from a black liquor recovery boiler contains large amounts of dust. The dust load varies between 40 and 75 kg per metric ton of dry solids (80 and 150 lb/ton). The dust is formed by the release of sodium from the bed to the flue gas over it. The amount of sodium released does not seem to depend on the sodium content in the black liquor dry solids.

The sodium and sodium salts in the black liquor evaporate at a rate dependent upon their partial vapor pressures and the diffusion conditions. A few feet above the bed, solid salts are present as Na_2CO_3 even at very high partial pressures of SO_2. The Na_2CO_3 reacts later with SO_2 to form Na_2SO_3, which is then oxidized to Na_2SO_4 by the excess oxygen in the flue gas.

The excess oxygen and the content of SO_2 in the flue gas show a corresponding decrease in this temperature field according to complete analyses using gas chromatography on samples taken before the screen tubes, before the superheater, after the superheater, and after the boiler tube bank (6).

The dust will contain only Na_2SO_4 after the boiler if the content of SO_2 is in excess of what is necessary for the stoichiometric conversion of Na_2CO_3 to Na_2SO_4, and SO_2 will be present in the flue gas at the exit of the economizer. In the opposite case (too little SO_2), Na_2CO_3 will still be present in the dust after the boiler, and the SO_2 content will be zero or very low at the exit.

The partial pressures of H_2SO_4 and SO_3 in the flue gas are a function of the reaction conditions. The formation of SO_3 and H_2SO_4 can be increased considerably if fuel oil with a high content of vanadium pentoxide (V_2O_5) is fired in the char bed oil burners or in load carrying oil burners. The SO_3 and H_2SO_4 are probably absorbed on the dust particles, and the dust gets sticky. Dust containing Na_2CO_3 can also form sticky dust through adsorption of SO_3.

Rather high concentrations of H_2SO_4 and SO_3 were found when firing of sodium sulfite liquor. The SO_2 content in the flue gas can be as high as 0.5 percent, that is, more than 10 times that of kraft boilers. Corrosion has occurred in the tube bank on such boilers, but not on kraft boilers. Some instances of corrosion in the last part of the economizers for the low odor type of recovery boiler might have been caused by SO_3 and H_2SO_4.

Dust sampled from 400° C (750° F) down to 150° C (300° F) has been analyzed, and differences in the crystalline structure were found. These differences may explain some of the differences in bulk weight and handling characteristics of dust in the electrostatic precipitators at different temperatures, even when no sticky dust was observed.

Very small amounts of Na_2S (0.2 percent) have been found in both large and small dust particles. Large particles of the range 5-15 μm (2.0-5.9 $\times 10^{-4}$ in) could be disintegrated ash from the combustion of very small drops or agglomerated sublimation products. Smaller particles, down to 1 μm (3.9×10^{-5} in), were analyzed, and the smaller ones of these probably could only have formed by sublimation. The smaller particles had about the same Na_2S content, which was probably a product of reaction between Na_2CO_3 and H_2S or elemental sulfur.

The dust containing Na_2S has no odor at normal atmospheric conditions. H_2S, however, is generated when the dust is exposed to CO_2 and water or water vapor. This fact can explain the occurrence of kraft odor at some distance from the mill when there is almost no odor at the mill site.

NaCl may be present in the dust if the black liquor contains chlorides. The HCl and chloride in the flue gas will probably react with Na_2SO_4 in the lower temperature range. It is possible to collect a substantial amount of HCl by scrubbing the flue gas with water. Sodium chloride condenses at lower temperature than Na_2SO_4, and this dust is, therefore, likely to have a smaller diameter than the Na_2SO_4 particles in the dust.

Iron can be found in the dust deposits on the tubes at what would be an alarming concentration if it were caused by corrosion in the boiler. Iron compounds exist, however, with a relatively high partial pressure at the temperature of the primary and secondary combustion zone and their evaporation is possible, with condensation taking place on the cooler surfaces in the boiler and economizer.

10.3 Different Recovery Boiler Designs

The present design of recovery boilers was developed in North America essentially by B&W and CE. Manufacturing overseas was by allied companies or licensed boiler manufacturers and to some extent by independent boiler manufacturers. The main differences between the two American boiler types are in the air supply, the spraying of the black liquor, the smelt discharge, and the design of the direct contact evaporator for the final concentration of the black liquor.

Another approach was often chosen in Scandinavia, with no direct contact evaporators for recovery boilers. The black liquor was evaporated to the final concentration in multiple-effect evaporators, and large economizers were used for cooling the flue gas before the electrostatic precipitators. The reason for this approach was the high cost of fuel and power.

Changes in the American design were necessary to produce odor free operation. The high ratio of the value of the recovered chemicals to recovered heat, and the very low price of fuel in North America made it economically feasible to run the recovery boilers with incomplete combustion. The deficit in steam generation was made up by oil- or natural gas-fired boilers at a comparatively low capital cost. The incomplete combustion sometimes caused very high emissions of H_2S. The direct contact evaporators were another source of H_2S, which was formed by the reaction:

$$2NaHS + CO_2 + H_2O \rightarrow Na_2CO_3 + 2H_2S$$

The latter source could, however, be eliminated by oxidation of the black liquor, that is, by converting the Na_2S to $Na_2S_2O_3$ by air or molecular oxygen in contact with the black liquor ahead of the multiple-effect evaporation. This practice, however, would not eliminate the generation of H_2S in the boiler itself. It would instead have a slight effect in the opposite direction by decreasing the heat value of the black liquor. This would lower the temperature in the primary air combustion zone and move the chemical equilibria toward forming more H_2S and S, and less SO_2, from the bed.

The two North American manufacturers proceeded in different ways to achieve odor-free operation in the cases where complete oxidation was not used. B&W adopted the design with a large economizer instead of the direct contact evaporator. CE has also tried other approaches to the problem. The Scandinavian manufacturers have generally kept their design, with small refinements.

10.3.1 Babcock & Wilcox (B&W) Recovery Boilers

B&W recovery boilers used two different types of direct contact evaporators prior to the low odor era. These were cyclone evaporators and venturi evaporator-scrubbers.

A B&W recovery boiler with a cyclone evaporator is shown in Figure 10-14. The primary air is supplied through air nozzles placed around the circumference of the boiler at an almost constant height over the slightly inclined bottom of the furnace. The air nozzles are arranged in groups of normally 4-5 nozzles at the same height. The air flow pressure in each group can be controlled by a damper. The smelt is discharged at the front wall through watercooled smelt spouts.

Secondary air is supplied at the distance of about 2 m (6 ft) above the primary air nozzles (measured at the center) by a smaller number of nozzles. Secondary air is supplied on all four walls. Spray nozzles for the black liquor are placed in the front and rear walls above the secondary air level.

The nozzles can be tilted up and down, and they also have a sideways swinging motion. Tertiary air is supplied above the spray nozzles for the black liquor. The air to the three windboxes is supplied by one or two forced draft fans and steam coil air heaters with the pressure adjusted to the demand for the secondary or tertiary air. The air is throttled to the primary air windboxes to adjust the pressure to the correct level. Measurements of the air flows to the different windboxes are made after the steam coil air heater.

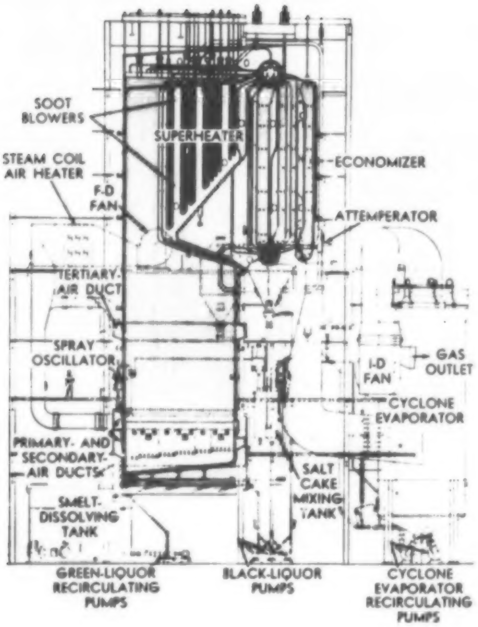

SOOT BLOWERS
SUPERHEATER
STEAM COIL AIR HEATER
F-D FAN
ECONOMIZER
ATTEMPERATOR
TERTIARY-AIR DUCT
SPRAY OSCILLATOR
I-D FAN
GAS OUTLET
CYCLONE EVAPORATOR
PRIMARY- AND SECONDARY-AIR DUCTS
SALT CAKE MIXING TANK
SMELT-DISSOLVING TANK
GREEN-LIQUOR RECIRCULATING PUMPS
BLACK-LIQUOR PUMPS
CYCLONE EVAPORATOR RECIRCULATING PUMPS

FIGURE 10-14

BABCOCK & WILCOX RECOVERY
BOILER WITH CYCLONE EVAPORATOR

The furnace is arranged with a rather large arch in the rear wall to distribute the gas in the superheater. Screen tubes are used ahead of the superheater to adjust the flue gas temperature to give the correct temperature of the superheated steam. The flue gas then passes the boiler tube bank and the economizer before exiting to the cyclone evaporator.

The cyclone evaporator is shown in Figure 10-15. The flue gas enters the cyclone tangentially near the bottom. Black liquor is sprayed across the gas inlet. The liquor drops are separated from the gas on its helical path to the outlet on the top of the cyclone. Black liquor is recirculated to nozzles at the top for wetting the walls. This wetting flushes the black liquor drops and dust, which have separated from the gas, to the sump tank in the bottom of the separator. Some control of the exit gas temperature or the final concentration of the black liquor can be exercised by adjusting the black liquor flow to the spray in the gas inlet. The operation resembles a low pressure drop venturi scrubber. The liquor is heated in a direct steam heater before it is sprayed into the furnace. The heater steam condensate dilutes the black liquor to a lower concentration than it had when leaving the direct contact evaporator.

The dilution of the black liquor is disadvantageous for heat economy, and it represents an explosion hazard if the black liquor injection into the furnace is interrupted temporarily and

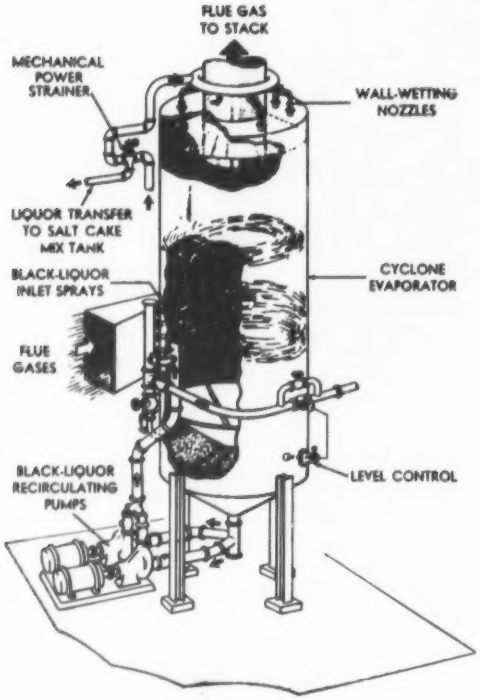

FLUE GAS TO STACK
MECHANICAL POWER STRAINER
WALL-WETTING NOZZLES
LIQUOR TRANSFER TO SALT CAKE MIX TANK
BLACK-LIQUOR INLET SPRAYS
CYCLONE EVAPORATOR
FLUE GASES
BLACK-LIQUOR RECIRCULATING PUMPS
LEVEL CONTROL

FIGURE 10-15
CYCLONE EVAPORATOR

the steam control to the direct heater should malfunction. Reheating of the black liquor using indirect heat exchangers has been done in Finland.

B&W introduced a boiler design with a large economizer to meet the demand for low odor generation (see Figure 10-8). The main difference from the previous design is that the height of the furnace was increased resulting in a proportional increase in the retention period for the combustion with tertiary air. Also, a large economizer was supplied for cooling of the flue gas to about 200° C (400° F) before the exit to the electrostatic precipitator. The economizer consists of long vertical tubes with a number of baffles arranged to give substantial crossflow for the flue gas. This arrangement increases the gas velocity and achieves better heat transmission than parallel flow. The crossflow arrangement seems to create some pockets with low gas velocity and to create some problems with the ash disposal with sootblowing, which is done with conventional retractable sootblowers.

10.3.2 Combustion Engineering (CE) Recovery Boilers

The CE recovery boilers were equipped with cascade evaporators before the requirement for reduced odor levels. A typical design is shown in Figure 10-16. The primary air was supplied

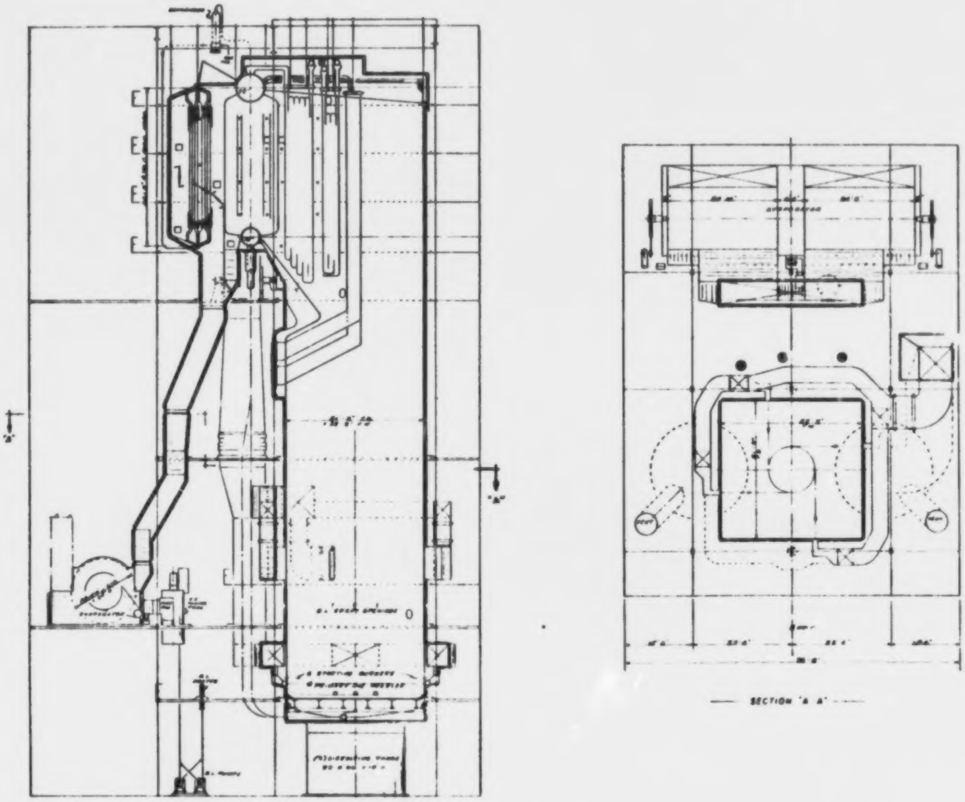


FIGURE 10-16

COMBUSTION ENGINEERING RECOVERY BOILER WITH CASCADE EVAPORATOR

at all four walls with primary air nozzles about 1 m (3 ft) above the bottom of the furnace. All primary nozzles were placed in a common windbox. The smelt was discharged through smelt spouts about 0.3 m (1 ft) above the bottom decanting hearth, which is horizontal.

Black liquor spray nozzles were placed about 6 m (20 ft) above the primary air nozzles on all four walls, with several nozzles per wall. The nozzles could be tilted up and down, but not swung sideways.

Except for the very first such boilers built, the supply of secondary air has been introduced at a distance of about 2.4 m (8 ft) above the level of the liquor sprays. The secondary air nozzles were divided into sections which could be shut off individually to allow for adjustment to the secondary air flow. Oil burners were, in some cases, placed in the secondary air windboxes for generation of steam in excess of that generated from black liquor combustion.

The furnaces were built originally without a nose at the rear wall under the superheater. A nose was added around 1960 to distribute the flue gases through the superheater. The superheater was made of panels with a side spacing of 30 cm (12 in) to improve the operating conditions of the superheater.

The gas passed the screen tubes, the superheater, the boiler tube bank, and the economizer to one or two cascade evaporators of the double rotor type. A cascade evaporator is shown in Figure 10-17. The rotors are constructed of tubes between the end disks and carry black liquor up through the flue gas pass. The gas velocity and the temperature determine the diffusion conditions and the evaporation rate to the flue gas. The time of exposure to the gas is considerably longer on the outer part of the rotors than on the inner part and may cause overdrying of black liquor at the outside of the rotors. This can be decreased by increasing the speed of the rotors. The residence time in the cascade is rather long (about four hours) compared to the cyclone evaporator. The variations in black liquor concentration caused by changes in the flue gas conditions should be damped by the large volume in the cascade. The concentration is normally controlled by bypassing the economizer with more or less flue gas through a damper or by diluting the black liquor with weak black liquor.

The demand for low emissions was met by CE with the introduction of the air cascade (see Figure 10-18). The direct contact with the flue gas was eliminated by using the combustion

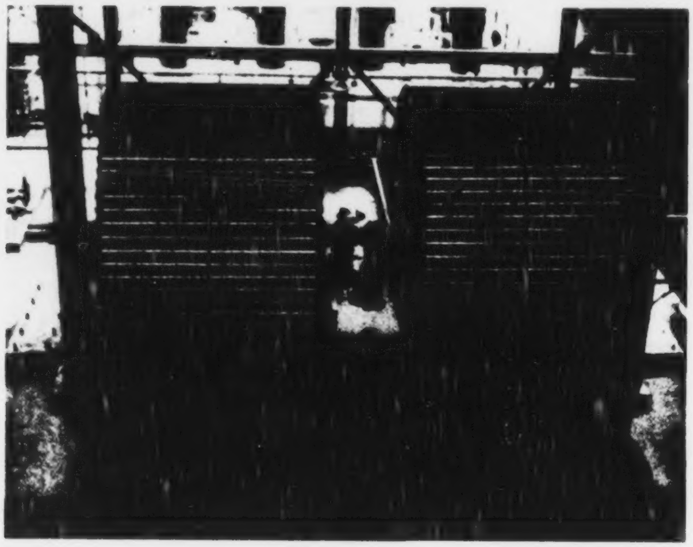


FIGURE 10-17
OPEN VIEW OF CASCADE EVAPORATOR

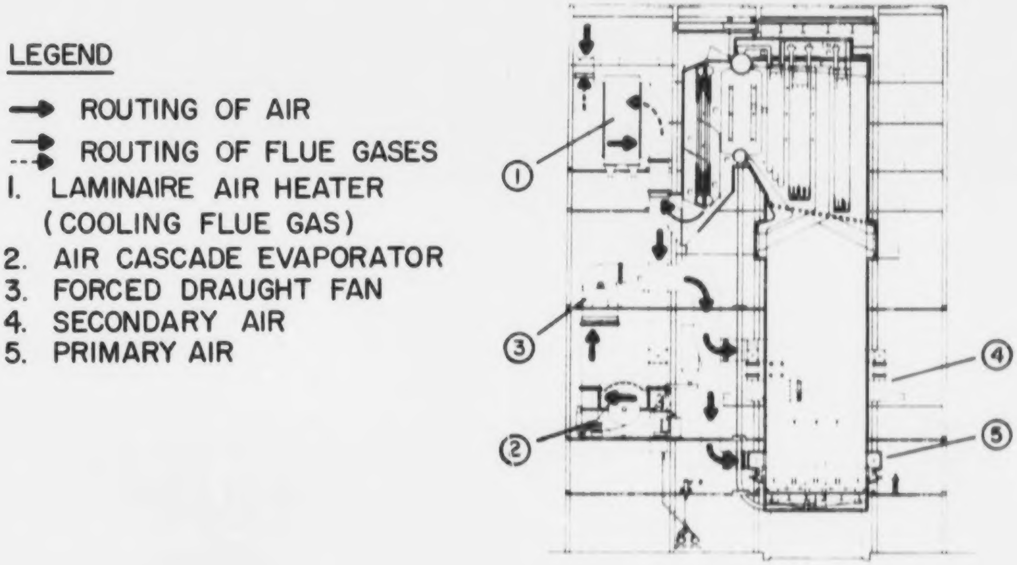
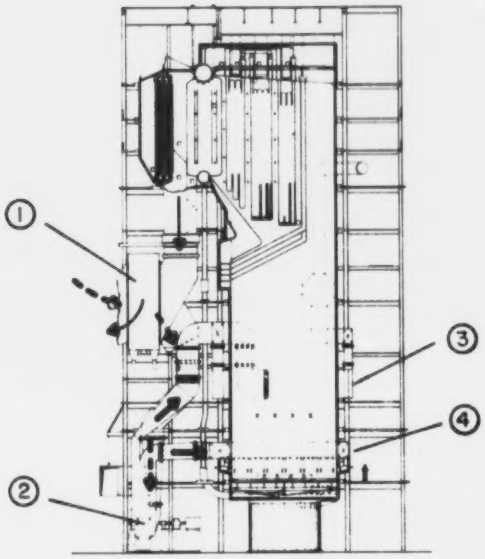


FIGURE 10-18

COMBUSTION ENGINEERING RECOVERY BOILER WITH
CASCADE EVAPORATOR ACE SYSTEM

air for the direct contact evaporation. This system is called ACE. The air was heated to 400-425° C (750-800° F) by rotating air heaters of the Ljungstrom type. This system had the disadvantage that the air to the furnace carried all the evaporated water vapor from the black liquor and so increased the humidity ratio by about 0.1 kg H_2O/kg dry air (0.1 lb H_2O/lb dry air). The increase in the partial pressure of the primary air increases the endothermic reaction between CO and H_2O to form CO_2 and hydrogen (H_2) at the contact with the bed. The temperature in the primary air combustion zone would, consequently, decrease, and tend to increase the emission of sulfur to the gas and increase the ratio of H_2S to SO_2. The lower temperature also would tend to decrease the reduction of the smelt.

A more recent development is shown in Figure 10-19. Recovery boilers of this type use large rotary air heaters to cool the flue gas to a temperature suitable for the electrostatic precipitators. The combustion air is heated to 315° C (600° F) to increase the temperature in the furnace, which increases the release of sodium, reduces the emission of sulfur from the bed, and decreases the ratio of H_2S to SO_2. This system is called LAH. The forced draft fans are placed after the heaters and are common for both primary and secondary air. This is disadvantageous in increasing power consumption and in decreasing the accuracy of air measurement.



LEGEND

⇉ ROUTING OF AIR
→ ROUTING OF FLUE GASES
1. LAMINAIRE AIR HEATER
2. INDUCED DRAUGHT FAN
3. SECONDARY AIR
4. PRIMARY AIR

FIGURE 10-19

COMBUSTION ENGINEERING RECOVERY BOILER WITH LAMINAIRE AIR HEATER & COMPLETE MULTIPLE EFFECT EVAPORATION L.A.H. SYSTEM

The final evaporation stage is made in a special type of concentrator following the multiple effect evaporator to reach 65 percent dry solids before the hopper and filter ash are added. The influence on the emissions at the high air temperature was very favorable. The theory predicts a greater evaporation of sodium and a decrease in the H_2S/SO_2 ratio above the bed. The results of the operation seem to verify this prediction; however, difficulties were encountered with the cleaning of the air heater because of narrow spacing between the regenerator elements. Frequent water washing was required. The air heaters were dimensioned for operation with 80 percent boiler load on one air heater, while the other heater was out for washing. The water washing may prove to be too troublesome for the operation and may cause some extra corrosion problems similar to those experienced in Scandinavian water washing of gilled tube economizers used before 1960.

CE now has designed recovery boilers (see Figure 10-9) that include large vertical steel tube economizers. The economizers are built in two or three passes with an open space between two consecutive passes. The flue gas passes downward parallel to the tubes and upward in the empty space between the tubes. The pressure drop is relatively low even with high gas velocities, and the steam used for sootblowing can be kept at a minimum. Finned tubes are often used with this design to enlarge the heat transmission surfaces of the tubes. This type of economizer has previously been used in Scandinavia with very good results.

10.3.3 Scandinavian Recovery Boilers

The design of recovery boilers in Sweden and Finland beginning with the first injection-type boiler included an economizer followed by an air heater for the cooling of the flue gases to 130° C (260° F). Such cooling was achievable when the heating surfaces were "technically clean." This design was chosen because of high fuel prices. The large dust load of the gas meant that the economizer and air heater often had to be water washed, even with continuous shot cleaning. Washing periods between 5 and 21 days were standard. The differences in the cleaning cycles were probably due to acid dust caused by high excess air: however, the influence of acid dust was not known at the time. The water washing damaged the economizers and they had, on the average, to be rebuilt every 10-15 years. The recirculation air heater, Figure 10-20, was used to decrease the corrosion of the air heaters in the "cold corners." The introduction of the hot precipitator in 1957 (placed between the boiler tube bank and the economizer) solved the problem of keeping the economizers clean without water washing, but it was more difficult to keep the precipitator in operation for long periods without shutdowns for cleaning. The long steel tube economizers were chosen after 1967, when the precipitators had to be designed for high collecting efficiency for particulate emissions and trouble free operation.

A typical Scandinavian recovery boiler is shown in Figure 10-21. It is manufactured by Götaverken Ångteknik AB (G.V.), Sweden, a licensee of B&W, England. Other manufacturers of recovery boilers in Scandinavia include Svenska Maskinwerken AB, Sweden, Oy Tampella AB, Finland, and A. Ahlström Osakeyhtiö, Finland.

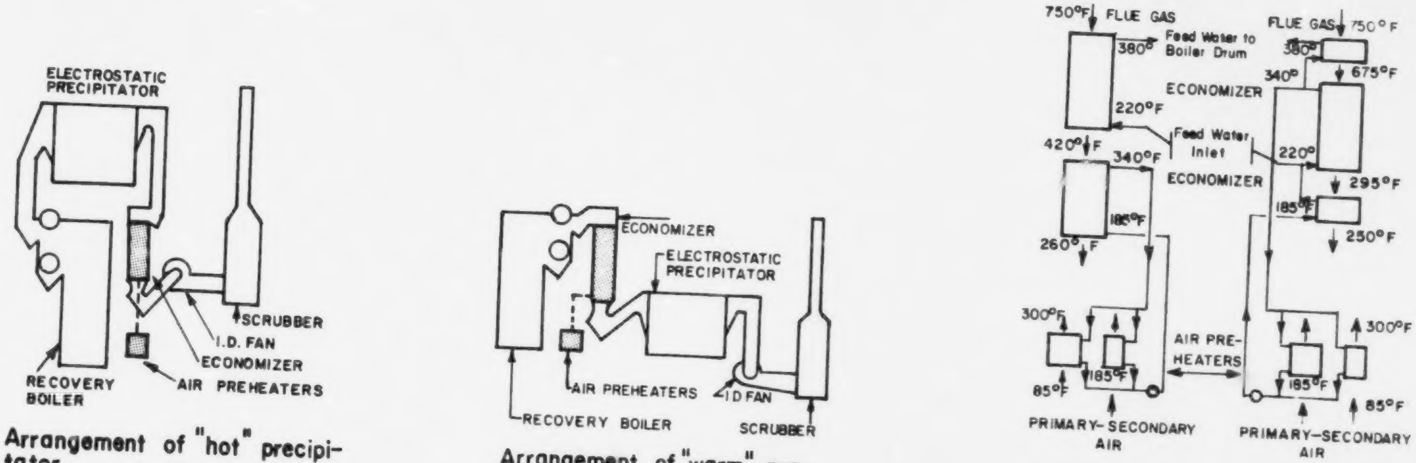
A comparison between the North American (Figures 10-14 through 10-19) and the Scandinavian standards (Figures 10-20 and 10-21) are shown in the preceding illustrations. The outstanding features in the Scandinavian design are as follows:

1. The primary and secondary air flows are handled by separate fans and air heaters, A, B.

2. The suction ducts to the fans are conveyed from the top of the building to give straight ducts, C, D, for an accurate measurement of the gas flow. This also is advantageous for ventilation since all recovery boilers in Sweden and Finland are built indoors because of the cold climate.

3. The primary air is split between low primary air, E, in the conventional windboxes and high primary air, F, in windboxes at a higher position and at a higher pressure through a booster fan (Götaverken).

4. The secondary air is split between low secondary air, H, on all four walls below the sprayer level and high secondary air, I, (Tertiary air) above the sprayer level.


ELECTROSTATIC PRECIPITATOR
SCRUBBER
I.D. FAN
ECONOMIZER
AIR PREHEATERS
RECOVERY BOILER
ECONOMIZER
ELECTROSTATIC PRECIPITATOR
AIR PREHEATERS
I.D FAN
RECOVERY BOILER
SCRUBBER
750°F
FLUE GAS
380°
Feed Water to Boiler Drum
ECONOMIZER
220°F
420°F
Feed Water Inlet
340°F
ECONOMIZER
185°F
260°F
300°F
85°F
185°F
AIR PRE-HEATERS
PRIMARY-SECONDARY AIR
FLUE GAS
750°F
380°
340°
675°F
220°
295°F
185°F
250°F
300°F
185°F
85°F
PRIMARY-SECONDARY AIR

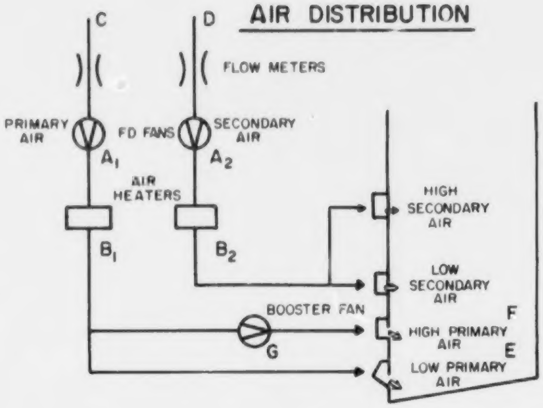
Arrangement of "hot" precipitator

Arrangement of "warm" precipitator

Arrangement of heating surfaces in economizer-air preheaters. Left, old system; right, new system (after 1956)

FIGURE 10-20

RECIRCULATION AIR HEATER FOR SCANDINAVIAN RECOVERY BOILER


AIR DISTRIBUTION
C
D
FLOW METERS
PRIMARY AIR
FD FANS
SECONDARY AIR
A_1
A_2
AIR HEATERS
B_1
B_2
HIGH SECONDARY AIR
LOW SECONDARY AIR
BOOSTER FAN
F
HIGH PRIMARY AIR
E
G
LOW PRIMARY AIR

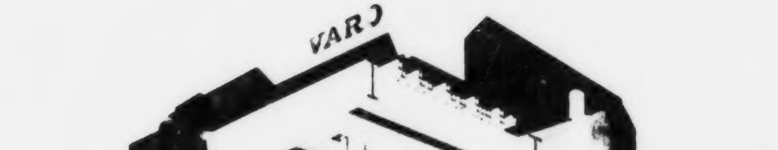

VARO
M
C
N
O
K_1 L
B_1
F
E
A_1
G

FIGURE 10-21

TYPICAL GÖTAVERKEN ÅNGTEKNIK RECOVERY BOILER

5. The cooling of the flue gases after the boiler tube tank is made with a long vertical steel tube economizer in several passes.

6. The gas flow is from the top of the tube baffle down to the bottom, which facilitates the ash transport at sootblowing (same as CE).

7. The flue gas is normally cooled to 160° C (320° F). This has been found to be the economic temperature for steam generation, the cost of the economizer and cost of the precipitator, and the power consumption in the induced draft fan.

8. The ash handling in the hoppers of the recovery boiler tube bank and the economizer banks, and in the precipitator, is of the dry type. Drag chain conveyors of a special design (Redler) are used. Rotary valves are used for sealing of the gas passage at the discharge of the ash. The ash from the hoppers is conveyed to the mixing tank with vertical dust chutes.

9. To avoid leakage of water vapor up into the dust chutes, which causes clogging, small screw conveyors are inserted before the mixing tank and equipped with air jet seals.

10.3.4 Rebuilding of Old Recovery Boilers to Low Odor Design

An existing recovery boiler with a direct contact evaporator can be rebuilt to the low odor design by installing a feed water economizer, possibly combined with an air heater. This addition will eliminate the emission of odorous compounds from the direct contact evaporator, but not from the furnace when the furnace is overloaded.

The air supply system can be revised to achieve better control of the air supply and thus increase the capacity for complete combustion of black liquor dry solids.

The evaporation plant has to be equipped with a concentrator to increase the concentration of the black liquor to the recovery boiler department to 62-65 percent. The electrostatic precipitator capacity must be increased to correspond to the reduced emission of particulate matter allowed by regulations. The higher black liquor concentration will tend to decrease the flue gas flow, but the higher flue gas temperature increases the velocity of flow. The result is often an increase of about 10 percent in required precipitator capacity. Furthermore, the migration velocity of the dust is lower primarily because of the lower humidity of the flue gas. The dust collecting efficiency has to be upgraded to meet the regulations. A new full size precipitator or at least an additional precipitator has to be included in the rebuilding program. The additional dust collecting capacity may be achieved with a scrubber if there is a bleaching plant which requires hot water and if the stack plume caused by the lower exit gas temperature is acceptable.

These additions can be erected with the old equipment in operation, and they can be ducted to the existing small economizer and the ID fan in a few days, if local conditions are favorable. The costs for lost production caused by downtime will then be limited to acceptable figures. This approach is probably the least expensive way to get low odor operation (16).

The usage of an existing recovery boiler for bark- and oil-firing after suitable changes is possible if a new modern recovery boiler is built in combination with an increase in production. The losses are then restricted to the special equipment for black liquor firing and the green liquor system. The life expectancy for a boiler converted to oil and/or bark firing is, in many cases, greater than if the boiler were kept on-line as a recovery boiler.

10.4 Process Variables

10.4.1 Objectives of the Recovery Boiler Process

The main purposes of the recovery boiler operation in the ordinary kraft process are:

1. Recovery of chemicals in the black liquor for dissolving into green liquor with all sulfur in the reduced state,

2. Generation of steam for the process in the mill,

3. Generation of steam with high pressure and high temperature to allow generation of power for the mill to the maximal extent,

4. Control of the combination to avoid emission of malodorous gases, SO_2, and particulate matter,

5. Allowing the use of the most inexpensive makeup chemicals available, and

6. Reliable operation with minimal capital, operating, and maintenance costs.

Exceptions to these general objectives are possible under certain circumstances. An example is cross-recovery between bisulfite or NSSC and kraft. The flue gases can, in this case, be scrubbed for recovery of SO_2 for production of the cooking acid for the bisulfite or NSSC process. The recovery process should then be operated to give sufficient SO_2 in the flue gas. This operation will decrease the sulfidity of the green liquor (and the white liquor from the recausticizing), and normally this decrease is favorable for a mill with small sulfur losses.

Some of the objectives given above are contradictory. For example, the generation of steam with a high pressure and temperature for the generation of power increases low capital and maintenance costs. The capital cost increases with pressure and temperature and so do the dangers of corrosion and increased maintenance costs. Another contradictory pair are avoidance of emission of SO_2 and low operational costs. Sulfur dioxide emissions can be avoided by evaporation of sufficient amounts of sodium to combine with the SO_2 in the gas, but this increased evaporation will increase the dust load in the gas and possibly increase the demand for sootblowing steam. It will also increase the size of the electrostatic precipitators needed.

Clearly then, the design of the recovery boiler must be the result of a balance between the different objectives and conditions, not only in the recovery boiler but also in the different departments which are influenced by or which influence the operation of the recovery boiler. Some of the operation and design parameters for normal kraft recovery boiler application are discussed in the following section.

10.4.2 Firing Rate for Dry Solids

Combustion of a given amount of black liquor solids produces a certain heat input in the recovery furnace. The combustion requires sufficient air for complete combustion and will produce an amount of flue gas that depends on the DS composition and amount of excess air. The temperature in the furnace will depend on four factors, the heat input from the dry solids, the preheated combustion air, the furnace dimensions and the operating pressure. The first depends on the production, on the type of wood species used for the mill, on the pulping yield, on the efficiency of the brown stock washing, and on possible oxidation of the black liquor. The second factor in the heat input can be varied from ambient air temperature up to 150° C (300° F) by heating the air with steam of 0.45 MPa and 1.1 MPa (50 and 150 psig) pressure. The air can be heated further by high pressure steam from the boiler to 230-260° C (450-500° F), depending on the pressure. This will give a slightly higher temperature in the furnace for improved operation or to compensate for a decrease in load. Heating the combustion air from the flue gas with indirect air heaters will increase the cost of the air ducts and would have an adverse effect at load changes (i.e., the air temperature would decrease when the black liquor heat input decreased). The air temperature will, on the other hand, increase with increased load; in which case decreasing its temperature, in some cases even to the extent of using ambient-temperature air, can offer a favorable solution.

The furnace dimensions must be chosen with some regard to the flue gas flow from combustion of the dry solids. The amount of dry flue gas from the organic content in the dry solids can vary considerably with different species and probably also with the rate of growth and the age of the wood and chip storage time. Changes in the inorganic content and the causticizing efficiency and reduction will cause only relatively small corrections. The furnace dimensions, therefore, depend not only on the total amount of dry solids but also on the composition of the black liquor. These factors should be taken into consideration if carryover of sprayed liquor droplets are to be avoided.

Sufficient retention time in the furnace and excess air are needed to achieve complete combustion before the flue gas enters the cooling tube surfaces. On the other hand, the oxygen content should not be too high to avoid the possible formation of sticky dust.

These factors and the conditions for the chemical reactions mean that it is impossible to operate a recovery boiler over a wide firing range. Incomplete combustion and further generation of H_2S will result if the boiler is overloaded, and a low reduction of the smelt and a high emission of SO_2 will result at a low load with low temperature in the furnace. The latter case can be avoided to some extent by increasing the heat input by firing an auxiliary fuel such as oil or natural gas in the char bed burners.

The average firing rate at which complete combustion can be achieved without frequent peaks above 1 ppm H_2S (with the black liquor concentrated to at least 62 percent dry solids) is, according to present observations, as follows:

Dry solids load per unit of furnace cross section, standard liquor conditions

1. American black liquor, 14,700 kg/m^2/day (3,000 lb/sq ft/day)
2. Scandinavian black liquor, 13,200 kg/m^2/day (2,700 lb/sq ft/day)

This difference is of great importance when the results from combustion in different countries are compared based upon economy and emissions of odor and particulate matter. There are, however, a number of cases where higher loads have been obtained with satisfactory combustion results. These results might depend on a greater attention to the operation of the boiler than can be expected as an average.

A great number of black liquor analyses have been investigated, both from North America and Scandinavia. The oxygen demand and the flue gas from the dry solids (the vapor from the black liquor has been excluded) at theoretical complete combustion without excess air varies considerably more for North American liquors than for Scandinavian:

Variation in Oxygen Demand and Flue Gas for Kraft Black Liquor Dry Solids

1. North American, ±19 percent
2. Scandinavia, ±8 percent

Normally there is a rather consistent linear relationship between the oxygen demand and the BHV for all fuels and organic compounds. The BHV is, however, determined with complete combustion to the oxidized state for all the elements and with the water vapor in the condensed state. The heat that is released in the recovery boiler is less than the BHV. Corrections have to be made for the reduction of the sulfur compounds, the heat of evaporation for the water in the black liquor, the water formed by the combustion of the hydrogen in the dry solids, and the heat of fusion for the smelt. It is, therefore, unlikely that there should be a consistent relation between the heat input steam and the air consumption, or between flue gas flow and the amount of black liquor dry solids fired.

The possibilities of reducing emissions by varying the dry solids firing rate in a recovery boiler are limited. The rated capacity for firing is determined after observation of the heat value and characteristics of the black liquor. The primary air flow for the rated capacity must be determined to give the correct temperature in the recovery boiler furnace in order to achieve the right proportions of sodium and SO_2 in the flue gas. This procedure probably leaves a rather small range of firing rates at the maximum load within which complete combustion without release of H_2S can be achieved. This range is about 5 to 10 percent and limits the possibility of variations of the operation on the upper side. Temporary load changes of greater magnitude must be covered by tank storage for black liquor and green liquor.

The range of load changes is also limited on the lower side. The relative amount of primary air and/or the temperature of the primary air has to be increased at a lower firing rate of dry solids to avoid emission of SO_2. Such corrective measures might allow operation down to 80% of the normal firing rate. The temperature in the primary air combustion zone will be too low at still lower loads without additional supply of heat by firing of oil or natural gas in the char bed burners. High emissions of H_2S (and elemental sulfur) can also take place in the primary air zone at low temperatures. Results from test runs indicate that if the H_2S release in the primary air zone is considerably above 200 ppm, even locally, it will be very difficult to achieve an H_2S concentration below 1 ppm in the exit from the boiler. It should be possible to get down to 65% of the normal dry solids firing rate with acceptable combustion and emissions with a substantial firing of additional fuel like oil or gas in the char bed oil burners to increase the temperature in the primary air zone.

Operation at reduced load of black liquor dry solids with additional fuel requires an even distribution of the additional heat input. Concentration of the heat supply from one or two burners can distort the configuration of the bed and cause carryover of organic material and combustion in suspension. Means to control the air to fuel ratio for the additional fuel should be provided.

The possibilities of operating recovery boilers at low load have not been investigated thoroughly. The high investment cost for the recovery boiler makes low load conditions rather unusual. The minimum load which can be recommended without causing unstable conditions in the primary air combustion zone, and without additional heat input from oil or natural gas, would be 80-100% of the maximum load with respect to SO_2 emissions and 65-100% with respect to H_2S emissions.

10.4.3 Black Liquor Characteristics

The most important characteristics of the black liquor in the design and operation of recovery boilers are:

1. Heat value and oxygen demand for complete combustion.
2. Viscosity and surface tension.
3. Organic/inorganic ratio and S/Na_2 ratio, and
4. Boiling point rise.

The heat value and oxygen or air demand for complete combustion are of utmost importance for both the proper design and proper operation of a recovery boiler. Attempts to achieve a usable formula for the heat value as a function of the elemental analysis have met with only limited success. The best solution seems to be to conduct laboratory cooks to the desired degree of delignification and bomb tests on the test liquor.

The variability in the black liquor composition with different wood species is related to the relative proportion of lignin and carbohydrates, and the type of carbohydrates, present in the different species (17, 18). Appendix 10-2 shows the composition and the BHV for softwood lignin, hardwood lignin, and carbohydrates, and the oxygen demand required for complete combustion. The composition and heat values have then been approximated for dry solids with a normal content of chemicals.

The amount of heat that will be released in a reducing atmosphere, that is, the "efficient heat value in reducing atmosphere," and the "resulting heat value of black liquor" (the total released heat used for steam generation) assuming no losses from the flue gas, have also been calculated. The values are shown in Figure 10-22 as a function of the oxygen demand. Three lines through the origin are shown. The deviation from a linear relation is shown as a percent. The BHV show the smallest deviations; however, these deviations are of the same magnitude as the allowable variations in the excess oxygen. The two lower lines in Figure 10-22, which show the heat released in a reducing atmosphere and the total heat available for steam generation, show a very good linear relationship, but the carbohydrates have great deviations from the lines through the origin.

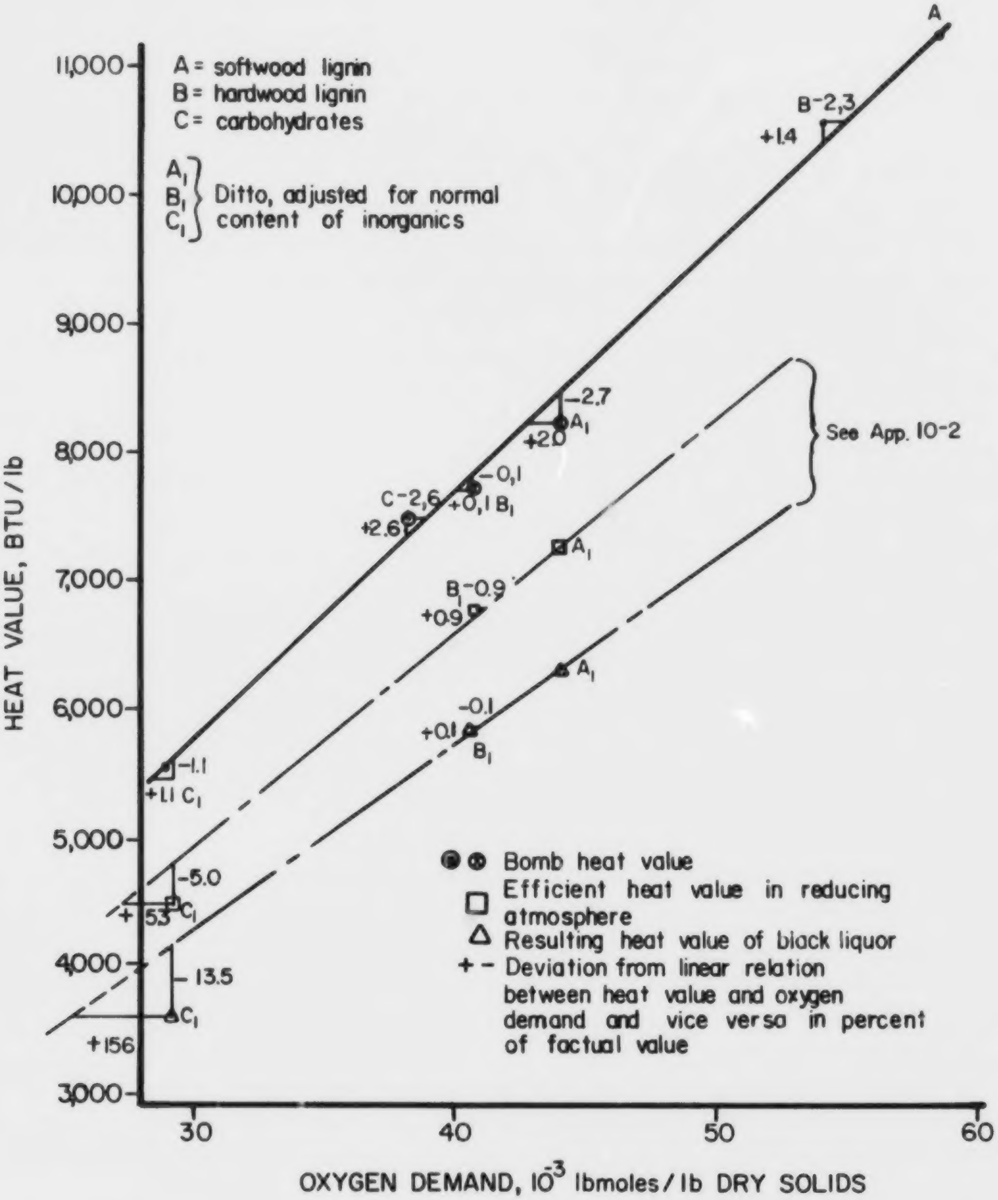


FIGURE 10-22

HEAT VALUE VS. OXYGEN DEMAND AT COMPLETE COMBUSTION

Variations in the lignin content in the wood, the amount of extractives and differences in the cooking process, variations in climatic conditions and the age of the trees before harvesting, and other variables might explain the great variations in the composition of the black liquor dry solids from different mills. Consideration of both the variations in the dry solids content and the BHV when comparing various firing rates seems to be more accurate than considering dry solids content alone.

The viscosity of black liquor as a function of the temperature is shown in Figure 10-23 (19). Very great variations were observed between different mills using the same species of wood. The viscosity is of great importance for the spray pattern. Liquor from eucalyptus pulping has, as an example, such high viscosity that the black liquor concentration is often limited to 60 percent to achieve a reasonably good, stable distribution of spray.

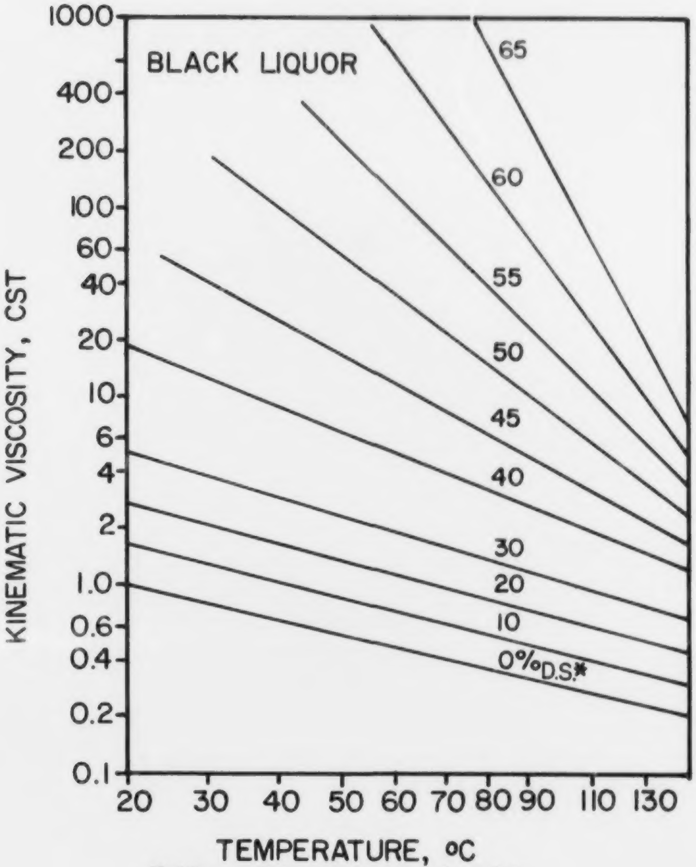
The surface tension seems to have little influence on the spray pattern. Investigations made with additives to decrease the surface tension in order to improve the spraying showed without significant changes.

The inorganic/organic ratio affects the heat value per pound of dry solids and complicates the operator's efforts to keep the load of the recovery boiler constant. The variations in the inorganic-organic ratio cause variations in the smelt flow and green liquor production. Such variations may decrease the reduction, as a high inorganic content often is a result of a temporarily low causticizing efficiency and reduction.

The molar ratio S/Na_2, along with the concentration of sulfur and the temperature, probably determines the release of sulfur from the bed. The ratio should, therefore, be kept as nearly constant as possible. In some plants, both the supply of makeup salt cake and also the spent acids from the ClO_2 generation and the tall oil plant are added continuously at a constant rate. The ash transport from the ash hoppers in the boiler and the economizer can be equalized to some extent by adjusting the sequence of the sootblowers to give a more steady supply of ash from different parts. The scraper conveyors used in Scandinavia, as compared to the common black liquor flushing system used in North America, tend to give a steady supply of ash.

The boiling point rise is a function of the inorganic/organic ratio and the concentration. The black liquor is normally sprayed into the furnace with a temperature near the boiling point. Changes in the spray pattern will follow a decrease in the boiling point rise if the temperature is kept at a constant value. An increase in the fraction of fine drops, which will cause carryover, will be the result of spraying at a temperature above the boiling point.

The boiling point rise is sometimes used for determination of the black liquor concentration. This method gives inaccurate results because of the variations in the inorganic/organic ratio.



*Where DS is dissolved solids

FIGURE 10-23

VISCOSITY OF BLACK LIQUORS (19)

10.4.4 Black Liquor Oxidation

Black liquor oxidation was discussed in Chapter 9. Oxidation of the black liquor with air converts the sulfide sulfur to thiosulfide. The importance of this oxidation to the recovery boiler process is that remaining sulfides react with CO_2 in the flue gas to form H_2S on contact. H_2S is also produced from sulfides on contact in a wet precipitator and a wet ash conveying system. This latter release, however, is insignificant compared to that from direct contact evaporation. The generation of H_2S on direct contact with the flue gas is totally eliminated with complete oxidation; however, oxidation tends to increase slightly H_2S generation in the furnace.

The decrease in heat value of the dry solids caused by black liquor oxidation leads to a decrease in the temperature in the furnace. The lower temperature decreases the ratio of H_2S and sulfur to SO_2, but increases the total sulfur release.

Investigations of the influence of oxidation are difficult because not only the sulfide sulfur but also the organic matter is oxidized. Some volatile compounds are stripped from the liquor, and the addition of oxygen increases the weight of the dry solids. Dry solids with 4 percent sulfur content increase in weight at complete oxidation by 2.5 percent.

Water is evaporated from the black liquor on contact with the air during oxidation. The heat consumption for this evaporation is quite high, about 3270 kJ/kg, (1400 BTU/lb) as compared to 486 kJ/kg (210 BTU/lb) in a conventional 6-effect evaporator. Furthermore, the black liquor is cooled in the direction of the wet bulb temperature, and this heat has to be replaced in the evaporating plant. The loss in heating valve caused by the oxidation of Na_2S to $Na_2S_2O_3$ must be replaced in the furnace.

The loss in heat value per unit mass of original dry solids almost doubles if the oxidation efficiency is increased from 90 to near 100 percent (20). The heat losses in steam generation can be calculated as 116 kJ per kg of dry solids (50 BTU/lb) per each percent sulfur for 90 percent oxidation and 209 kJ per kg of dry solids (90 BTU/lb) per each percent sulfur for 100 percent oxidation. Allowances are made for the evaporation in the oxidation towers as compared to evaporation in a 5-effect evaporator. This heat loss might gain in importance with the increased sulfidities resulting from recovering the malodorous gases and with increased fuel prices.

The oxidation decreases the air consumption by 1-2 percent but the heat input has a greater influence on the furnace temperature. The primary air temperature must be increased to compensate for the lower heat value and to keep the reaction condition constant in the primary air zone with use of fully oxidized liquor.

10.4.5 Air Distribution and Air Temperatures

The air distribution, the air temperatures, and the spraying pattern are the main independent variables by which the operation of the recovery boiler can be changed. The specific load, expressed as dry solids per unit cross section of the furnace, depends on the dimensions of the recovery boiler and the production of the pulp mill. The heat value of the dry solids of the black liquor depends on the type of pulp and the species of wood used for production.

The total amount of air which can be used for the combustion under the present technology has both lower and upper limits. The lower limit is set by the condition that at least 10 percent excess air has to be used to avoid unburned matter in the flue gas and formation of H_2S. The upper limit of about 20-25 percent excess air is necessary to avoid the possible formation of SO_3 in the flue gas, and the resultant sticky dust caused by SO_3 adsorption on the dust. A certain amount of the total air must be used for the primary air combustion zone to give the proper oxygen concentration in this zone and to give the correct temperature. With the present recovery boiler designs, the correct amount for primary air is approximately 60 to 70 percent of the theoretical amount of air for complete combustion without excess air. The reduction of the sulfur compounds in the smelt is probably enhanced by a low oxygen concentration and a high temperature, within certain limits. An increase in the amount of primary air increases both the oxygen concentration and the temperature. The two parameters of oxygen and temperature are evidently coupled together, and some combination of them must exist that is the most favorable.

The air is currently heated either by steam from the backpressure turbine at pressures of 1.13 MPa (150 psig) and 0.45 MPa (50 psig) or with feedwater recycled from the top of the economizer through air heaters and fed back to the inlet of the economizer (Figure 10-20). The most economic choice depends on the prices of fuel and power at the specific site. The steam air heaters give an increased flow of high pressure steam through the turbine and increase the back pressure power generation. The recirculation air heater permits a lower capital cost for the economizer for the same flue gas exit temperature. This latter system is a very clean and easily operated arrangement, but limits the air temperature to about 150° C (300° F). Possible ways to increase the air temperature are either to return to using the indirect type of air heater with cooling of the flue gas by air or to use a rotary Ljungstrom type air heater. The Ljungstrom type air heater requires rather extensive ducting of the hot air from the heaters to the furnace. Direct heating by firing auxiliary fuel after the steam coil or recirculation air heaters is possible. The water vapor from the additional fuel will change the equilibrium conditions for the endothermic water gas reaction, which is only partly compensated by the increase in the partial pressure of CO_2. This method works the same way as firing oil in the furnace with the char bed burners, which is favorable at low load conditions. The primary air velocity is increased, tending to increase the evaporation of sodium.

Advantages in raising the primary air temperature are:

1. Velocity for the same flow of air increases and therefore improves the sodium evaporation from the bed,

2. Release of sulfur from the bed decreases,

3. Distribution of the released sulfur changes in the direction of more SO_2 and less H_2S, and

4. Decreasing the primary air flow is possible, and consequently, more air is available for the secondary air supply.

Adjusting the velocity and distribution of the primary air flow within the furnace is probably valuable so that the flow corresponds to the black liquor distribution. B&W

designed a system with an adjustable nozzle, which was used around 1960 in the United States, but it was abandoned. This system has, however, been used in Scandinavia (see Figure 10-24) as standard equipment.

The difference between the total air flow and the primary air flow is used as a computation of secondary air to complete the combustion. Assuming an average figure of 115 percent of the theoretical air as the total combustion air, and 70 percent used as primary air, only 45 percent is available to complete the combustion. This small amount has to cover the whole cross section of the furnace and effects good mixing of the combustible gas with the air. The suppliers of recovery boilers all use different ways of achieving complete combustion. They all seem to work provided that a reasonably low amount of H_2S is present in the gas mixture coming from the primary air combustion zone.

Jones, Brink, and Thomas suggest that another method of controlling the combustion conditions is to supply oxygen to the air (21, 22). This tends to reduce the volume of the combustion chamber and to allow the temperature to be increased to the desired level. But

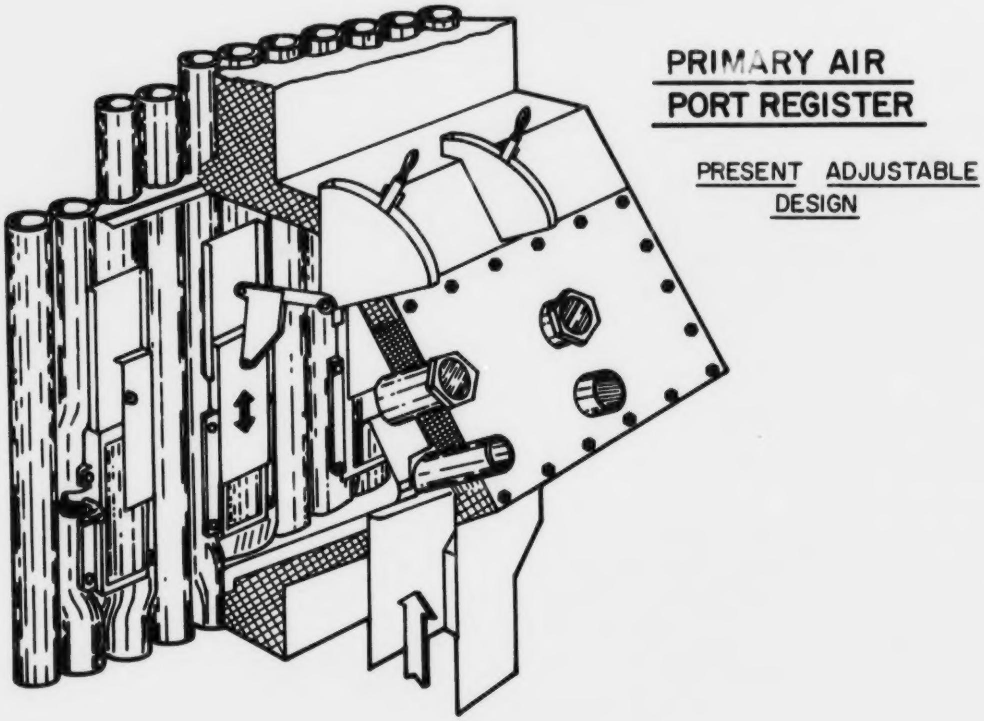


FIGURE 10-24
ADJUSTABLE AIR PORTS

there are some economic drawbacks. The amount of flue gas per unit of steam generated is less. The superheating of the steam, which is of extreme importance for the back pressure power generation, is considerably more expensive and more complicated than with the present type of superheaters, because the flue gas temperature at the entrance to the superheater must be kept low enough to avoid very difficult slagging problems.

The greatest problem with oxygen addition is probably that of achieving a sufficient mixing of the gas from the primary air combustion zone with secondary air.

10.5 Diverse Obnoxious Compounds

CH_3SH, CH_3SCH_3, CH_3SSCH_3, carbonyl sulfide (COS), and carbonyl hydrogen sulfide (COSH) were measured in addition to H_2S, SO_2, and S in the lower part of the recovery boiler in the gas phase. They were not found to any measurable extent, however, in the upper part of the furnace in the neighborhood of the screen tubes where the boilers were operated with 2 percent excess oxygen. Some tests indicate that H_2S is present in rather high concentrations when CO and H_2 are also present in high concentrations. A very good correlation seems to exist between H_2S and H_2 content. Both H_2S and SO_2 emissions can be controlled to a satisfactory degree by applying present technology to the design and operation of recovery boilers as previously discussed (23).

The obnoxious compounds, according to available test results, present no problem in a reasonably well operated recovery boiler. CH_3SH, CH_3SCH_3, and CH_3SSCH_3 can, however, be stripped from the black liquor in the direct contact evaporators.

The NO_x emission from recovery boilers are probably of minor importance because of the low combustion temperatures that are reached even locally in comparison to the temperatures which are reached in the flames of oil and pulverized coal burners. The relatively high NO_x content which has been found after combustion of ammonium bisulfite (NH_4HSO_3) liquor, is probably caused by oxidation of the monatomic nitrogen produced by the cracking and combustion of ammonia.

10.6 Direct Contact Evaporation

Direct contact evaporation of black liquor is performed at most kraft pulp mills in the United States for concentrating the liquid from 40-50 percent to 60-70 percent solids (ash from precipitators and ash hoppers not included) to facilitate combustion in the recovery furnace. The normally used direct contact evaporators are the cascade, cyclone, and venturi evaporators. The direct contact evaporator can act as an air pollution source, but also in some aspects as an air pollution control device. A development by CE was the ACE system in which the black liquor is concentrated by the combustion air in a direct contact evaporator. The air is preheated by Ljungstrom air heaters to 400-425° C (750-800° F). The water vapor and any compounds released from the black liquor are carried with the combustion air to the furnace. This arrangement is called an indirect contact evaporator. The relative suitability of direct contact evaporation, as opposed to multiple-effect evaporation of black liquor, is based on operation and capital costs, flexibility with respect to capacity, and environmental aspects.

10.6.1 Specific System Characteristics

Direct contact evaporation can be performed in one of three different types of systems. One of the systems, the high pressure drop venturi scrubber with strong black liquor as the liquid medium, has the dual function of water evaporation and particulate removal. The venturi type evaporators are gradually being complemented with additional dust collectors or replaced because of their inability to meet particulate air pollution emission standards. The different types of direct contact evaporation systems employed are shown in Figures 10-14 through 10-17. The operating characteristics of recovery boiler flue gases, as indicated by moisture content, gas temperatures, and particulate loadings for the different types of direct and indirect contact systems for concentrating strong black liquor, are presented in Table 10-7.

TABLE 10-7
RECOVERY FURNACE EXHAUST GAS PROPERTIES FOR DIRECT AND INDIRECT CONTACT EVAPORATION SYSTEMS

	Direct Contact Evaporators			Indirect
Property	Cascade	Cyclone	Venturi	ACE
Pressure drop, in. w.g.	2-4	2-4	15-30	2-4
Flue gas temperature at:				
economizer exit, °C	315-370	315-370	315-370	315-370
(°F)	(600-700)	(600-700)	(600-700)	(600-700)
evaporator exit, °C	150-163	132-163	88-110	–
(°F)	(300-325)	(270-325)	(190-230)	–
Flue gas moisture content at:				
economizer exit, g/m³	5-9	7-11	7-11	7-11
(gr/cf)	(2-4)	(3-5)	(3-5)	(3-5)
evaporator exit, g/m³	2-7	5-9	0.9-1.0	–
(gr/cf)	(1-3)	(2-4)	(0.4-0.8)	–
precipitator exit, g/m³	0.1-1.1	0.1-1.1	–	0.07-0.2
(gr/cf)	(0.05-0.5)	(0.05-0.5)	–	(0.03-0.10)

The cascade- and cyclone-type direct contact evaporators are low pressure drop gas-liquor contact devices that are used for concentration of strong black liquor by evaporation. Electrostatic precipitators, located downstream of the direct contact evaporator, provide particulate emission control and chemical recovery with these low pressure drop systems. Cascade evaporators employ a rotating cylindrical drum with attached tubular wheels perpendicular to the direction of the gas stream for gas-liquid contact and are normally used with recovery boilers manufactured by CE. Cyclone evaporators are basically low pressure drop cyclonic scrubbers for gas-liquid contact and are normally used with recovery boilers manufactured by B&W.

The direct contact evaporator serves several functions besides the concentration of black liquor to 60-70 percent solids. These functions include:

1. Reducing the inlet gas temperature to the electrostatic precipitator, where the lower gas temperature results in a reduced volume flow rate, which allows a smaller precipitator to be constructed at a lower capital cost;

2. Reducing the inlet particulate loading to the electrostatic precipitator by 20-40 percent by weight, primarily by scrubbing of large particles emitted from the furnace, as reported by Hisey (24);

3. Absorbing about 75 percent of the SO_2 emitted from the recovery boiler (25, 26), and nearly all of the sulfur trioxide (27); and

4. Absorbing H_2S emitted from the recovery boiler (28, 29, 30) under conditions of high black liquor pH and low sodium sulfide concentration in the strong black liquor.

10.6.2 Air Pollution Control

Direct contact evaporation has the potential for liberating substantial amounts of malodorous sulfur gases from the black liquor or for absorbing sulfurous gases generated from the recovery furnace. Considerable amounts of H_2S and lesser amounts of CH_3SH can be released from the black liquor by acidifying Na_2S and sodium mercaptide (CH_3SNa) by the action of acidic flue gas constituents, such as CO_2, SO_2, and SO_3. Organic sulfur gases, such as CH_3SCH_3 and CH_3SSCH_3, and malodorous organic nonsulfur compounds can be evolved from the heating of the black liquor by contact with recovery boiler flue gas (31).

Major variables affecting the potential for release of malodorous sulfur compounds from black liquor during direct contact evaporation include inlet liquid composition, liquid pH and alkalinity levels, inlet liquor and flue gas temperatures, and the degree of gas-liquid contact. Recent studies (28, 32) indicate a substantial increase in reduced sulfur emission levels to the stack, if sodium sulfide concentration is increased in the strong black liquor entering the direct contact evaporator. Therefore, a high black liquor oxidation efficiency must be obtained to reduce the Na_2S to between 0.01 and 0.1 g/l to minimize malodorous sulfur gas generation during direct contact evaporation. See Table 10-8 (33).

TABLE 10-8
EFFECT OF BLACK LIQUOR OXIDATION ON SULFUR GAS EMISSIONS DURING DIRECT CONTACT EVAPORATION (33)

Sulfur Gas	Unoxidized Liquor		Oxidized Liquor	
	kg/t	lb/ton	kg/t	lb/ton
H_2S	2.5-15	5.0-30.0	0.05-1.0	0.1-2.0
CH_3SH	0.15-1.0	0.3-2.0	0.025-0.10	0.05-0.20
$(CH_3)_2S$	0.025-0.075	0.05-0.15	0.005-0.025	0.01-0.05
$(CH_3)_2S_2$	0.05-0.15	0.10-0.30	0.005-0.075	0.01-0.15

These findings have been verified in subsequent studies conducted by Martin (34).

Murray and Rayner (29) have shown that the liquid pH of the incoming black liquor can have a considerable impact on H_2S emissions during direct contact evaporation. Increasing the liquid pH reduces the rate of H_2S formation at any given level of sodium sulfide and results in a reduction in the amount of H_2S generated in the direct contact evaporator. See Table 10-9 (33).

Two additional variables are liquid alkalinity and gas-liquid contact. The presence of substantial proportions of carbonate ion in the black liquor at high pH of 12.0 or more gives the liquid a large potential buffering capacity against pH reductions caused by contact with CO_2 from the recovery furnace flue gas. Increasing the degree of gas-liquid contact may result in either a substantial increase or decrease in malodorous gas emissions, depending on the characteristics of the black liquor and the flue gas temperatures.

Under certain conditions, the direct contact evaporator can act as an air pollution control device to absorb H_2S from the recovery boiler combustion zone flue gases (28, 30, 32). A particular advantage in direct contact evaporation, where high degree black liquor oxidation is practical, is absorption of H_2S from the combustion zone during periods of recovery boiler upset.

TABLE 10-9
EFFECT OF BLACK LIQUOR pH ON H_2S EMISSIONS DURING DIRECT CONTACT EVAPORATION (4)

pH	Na_2S g/l	H_2S Concentration* Inlet	Outlet	Change
12.6	14.2	11	35	+24
12.3	18.3	27	122	+95
12.1	15.3	24	180	+156

*Computed in ppm by volume at 0° C and 760 mm Hg (32° F and 1.0 atm).

10.6.3 Complete Multiple-Effect Evaporation and Indirect Contact Evaporation Comparison

Indirect contact evaporation is used to concentrate black liquor from 50 to 60-65 percent solids to eliminate the possibility of odorous gas release during direct contact evaporation. Systems employing complete multiple-effect evaporation and indirect contact evaporation have been installed at new kraft mills in the United States and Canada (35, 36).

The multiple effect evaporation to the dry solids concentration used for injection into the boiler eliminates a potentially large source of malodorous sulfur gas emissions resulting from direct contact evaporation. The technique has proved successful in extensive experience in Scandinavia (37). Multiple effect evaporation to virtually eliminates the recovery furnace as a source of malodorous gas emissions. It is then only necessary to operate the recovery boiler so as to minimize sulfur gas emission. The Scandinavian system also has a lower moisture content in the exit gases from the recovery boiler than systems using direct contact evaporators, therefore reducing plume opacity caused by condensed water droplets.

Indirect contact evaporation can also reduce sulfur emissions, but by introducing the water vapor from the air cascade into the furnace, the combustion equilibrium conditions change and the temperature decreases in the primary air combustion zone. The air-cascade evaporation system may cause corrosion and particulate plugging of the rotary heat exchanger.

Direct contact evaporators tend to have greater heat economy than air cascade evaporators, but lower heat economy than complete use of additional multiple-effect evaporators (38). The difference in heat economy grows in importance with increasing fuel costs. An additional factor in direct contact evaporation is that high degree black liquor oxidation can reduce the heating value of black liquor by as much as 5 to 10 percent (39).

10.7 Flue Gas Scrubbing for Gaseous Emissions

Flue gas treatment with absorption of the malodorous gases would be an economical method of converting old recovery boilers to meet present standards for air pollution if it were not possible to rebuild the plant to the low odor system. This equipment can be erected after the precipitator during the operation of the boiler and connected in a reasonably short time if space is available. Any changes requiring a long downtime for the recovery boiler are prohibitive because of production loss. With fuel prices below $1.42 per million kJ ($1.50 per million BTU), it is almost never feasible to rebuild an existing unit to gain better heat economy even though a new design would be feasible for a new mill.

In an existing recovery boiler, it may not be possible to operate without release of SO_2 and H_2S. The existing direct contact evaporators can be used to absorb SO_2. The absorption of H_2S may also be possible, but in most cases insufficient to meet the regulations regarding emissions of this gas.

Methods and equipment have been designed for the absorption of H_2S. Three of these systems are commercially available. Only the last type has been installed in more than one mill. These systems are:

The B. C. Research Council absorption scrubber,

The TRS Weyerhaeuser absorption scrubber, and

The Gadelius-Misubishi absorption scrubber.

The B. C. Research Council's (B.C.R.C.) method uses a rather concentrated Na_2CO_3 solution for absorption of the H_2S (29, 40). The principle is that the carbonate concentration should be in equilibrium with the CO_2 partial pressure in the gas to avoid excessive loading with Na_2CO_3 and to avoid an increase in the lime consumption in the recausticizing department. The carbonate solution is sprayed at the top of a packed tower, and the liquor moves downward countercurrent to the flue gas.

The liquor is extracted at the bottom of the scrubber and is pumped to an oxidizing unit where Na_2S is converted to $Na_2S_2O_3$. Enough iron compounds are normally available in the remaining dust after the precipitator to act as a catalyst for a rapid conversion to $Na_2S_2O_3$. This conversion was observed during the operation of scrubbers for generation of hot water by heat recovery from flue gas (41).

The method is the property of B.C.R.C., and SF Products Canada, Ltd., manufactures and markets the equipment. It has been discussed in combination with heat recovery for generating hot water for the bleach plant, in which case the feasibility of the installation seems satisfactory, especially at the present level of fuel prices. The pressure drop on the flue gas side depends on the concentrations of H_2S and CH_3SH in the flue gas, as these determine the number of exchange units in the packed tower. One application was calculated at 750 Pa water (3 inch w.g.) pressure drop for reduction from 600 ppm to 5 ppm, and the same pressure drop for the heat recovery section. Compressed air is used for the oxidation unit. A bleed-off of the scrubbing liquor and fresh alkali make-up is necessary to maintain the correct liquor composition. A typical arrangement is shown in Figure 10-25.

The TRS System was developed and patented by the Weyerhaeuser Company (42) and uses a Nalco water solution of chelated ferric chloride in a proprietary formulation. The absorbed H_2S forms elemental sulfur, and a special packing is used to avoid plugging. This package was developed and is marketed by Fritz W. Glitsch & Sons, Inc.

The TRS-scrubber absorbs up to 99 percent of the H_2S and collects about 85 percent of the particulate matter. The resulting slurry of colloidal sulfur, salt, and other materials is passed through a thickening and washing operation for recovery of the sulfur. Soda ash and air are used to keep the solution neutral and to oxidize the Nalco water solution. The solids concentration is kept at about 20 percent by bleeding to the green liquor. The sulfur, salt, and Nalco solution are recovered. Several scrubber units are used in parallel; one can be taken out for cleaning, or the packing elements can be removed for cleaning. The pressure drop with all units in operation on the gas side is about 1250 Pa water (5 inch w.g.). A typical arrangement is shown in Figure 10-26. The above method has the advantage of removal of sulfur from the kraft process. Such removal may become a necessity in the future to keep the sulfidity of the white liquor in a range such that corrosion effects on equipment remain tolerable.

The Gadelius-Mitsubishi method uses one or two stages of spray nozzles in countercurrent arrangement to the flue gas flow for the absorption of H_2S in Na_2CO_3 or NaOH. Fresh alkali is used for the makeup of the absorbing solution. Several units are in operation in Japan. This scrubber has very low pressure drop on the gas side, about 245 to 375 Pa (1 to 1.5 inch w.g.). None of these methods will have a high absorption efficiency for CH_3SH, CH_3SCH_3, or CH_3SSCH_3. The absorption efficiency for the other sulfur compounds must, therefore, be quite great in some cases to bring the TRS down to the limits of the regulations. This fact should be considered at the design stages for flue gas scrubbing equipment.

Other methods for removing reduced sulfur compounds, such as scrubbing with an alkaline suspension of activated carbon, were suggested after laboratory studies of absorption (43, 44). The recently recognized importance of both increasing the furnace temperature in the

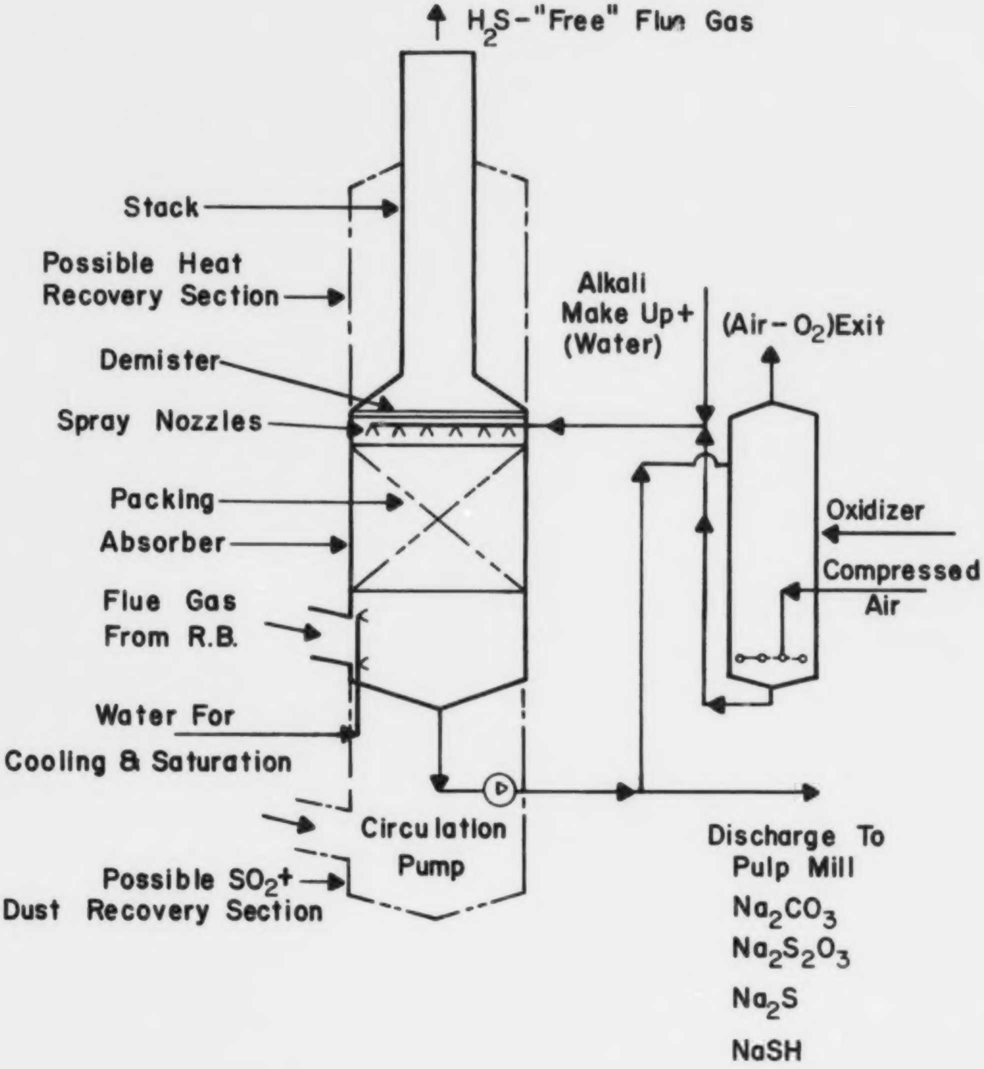

↑ H_2S-"Free" Flue Gas
Stack
Possible Heat Recovery Section
Demister
Spray Nozzles
Packing
Absorber
Flue Gas From R.B.
Water For Cooling & Saturation
Circulation Pump
Possible SO_2+ Dust Recovery Section
Alkali Make Up+ (Water)
(Air – O_2)Exit
Oxidizer
Compressed Air
Discharge To Pulp Mill
Na_2CO_3
$Na_2S_2O_3$
Na_2S
NaSH

FIGURE 10-25

BRITISH COLUMBIA RESEARCH COUNCIL DESIGN FOR H_2S ABSORPTION SCRUBBER

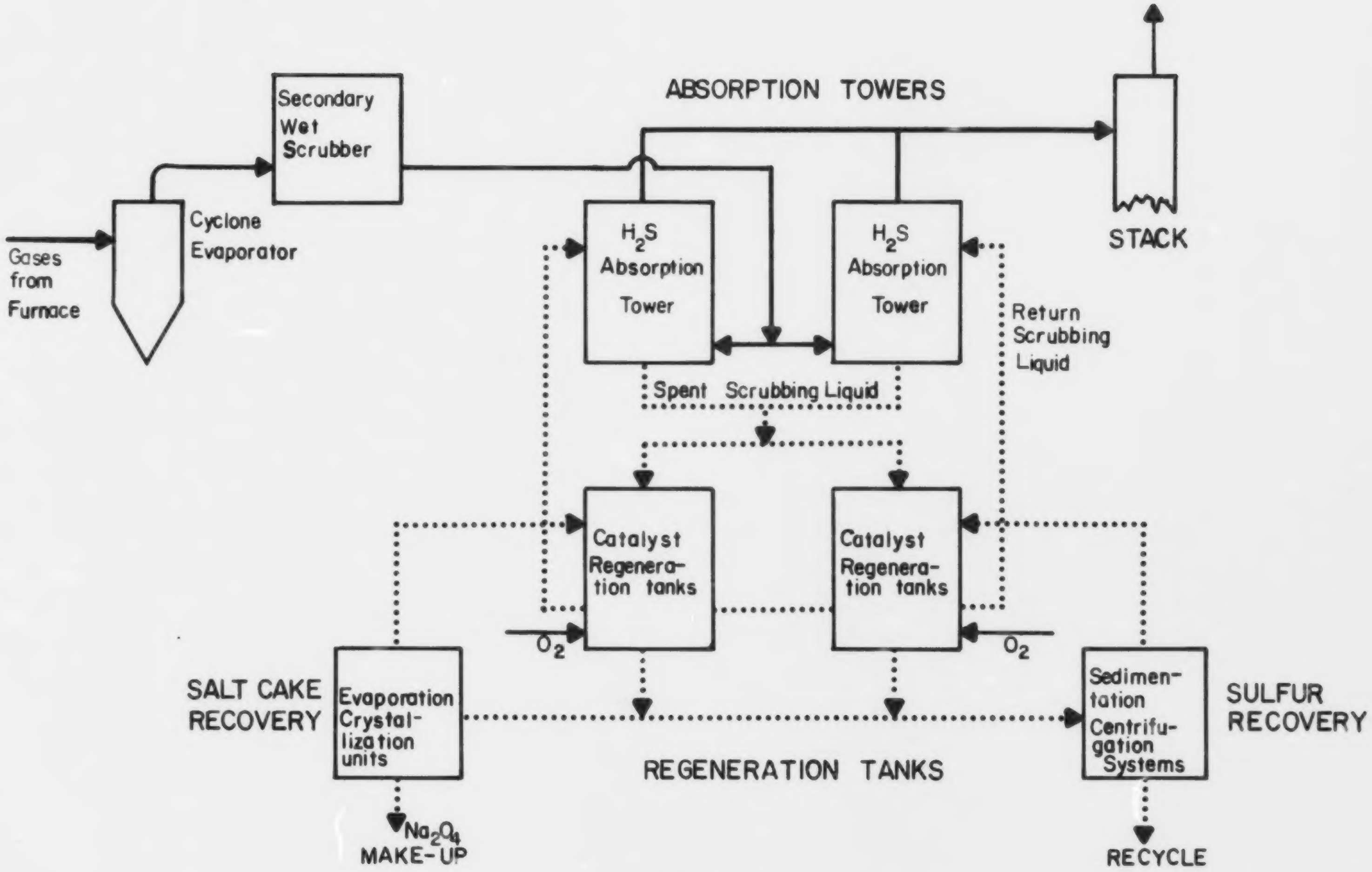
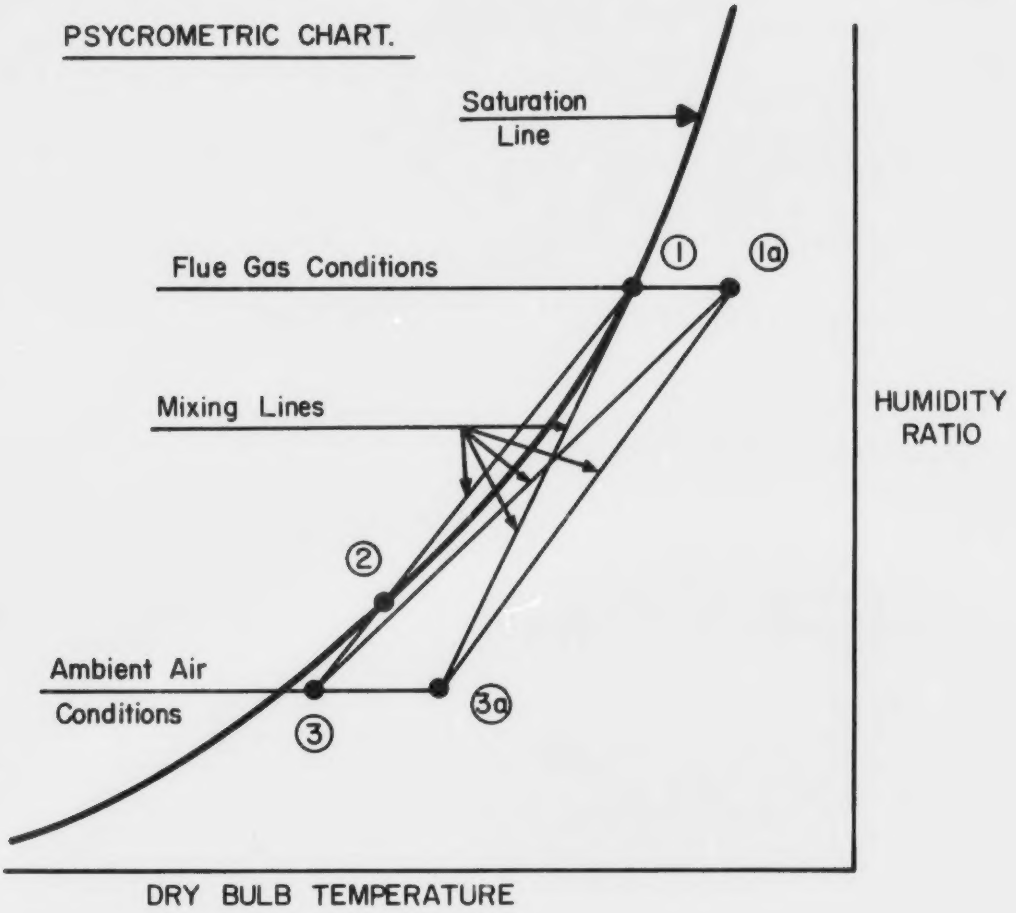

ABSORPTION TOWERS
Gases from Furnace
Cyclone Evaporator
Secondary Wet Scrubber
H_2S Absorption Tower
H_2S Absorption Tower
STACK
Return Scrubbing Liquid
Spent Scrubbing Liquid
Catalyst Regeneration tanks
Catalyst Regeneration tanks
O_2
O_2
SALT CAKE RECOVERY
Evaporation Crystallization units
REGENERATION TANKS
Sedimentation Centrifugation Systems
SULFUR RECOVERY
Na_2O_4 MAKE-UP
RECYCLE

FIGURE 10-26

GLITSCH-WEYERHAEUSER DESIGN FOR A TRS SCRUBBING SYSTEM


PSYCROMETRIC CHART.
Saturation Line
Flue Gas Conditions
①
1a
Mixing Lines
②
Ambient Air Conditions
③
3a
HUMIDITY RATIO
DRY BULB TEMPERATURE

The mixing lines show extention

Flue Gas Condition	1	1	1a	1a
Ambient Air Condition	3	3a	3	3a
Condensation	Yes From ① to ②	No	No	No

FIGURE 10-27

FORMATION OF VISIBLE PLUME THROUGH CONDENSATION OF WATER VAPOR primary air combustion zone to reduce the emissions of sulfurous gases (9, 11, 13, 14); and increasing the residual alkali to reduce the formation of some of the malodorous compounds, possibly needs further examination since this method can probably reduce the emissions of malodorous gases. These changes probably are easier to adopt operationally than an absorption system.

SO_2 can be removed from the flue gases by any of several designs of simple scrubbers. Two of these are the SF Scrubber-Modo System and the Warkaus scrubber (45), which is a double venturi scrubber arranged with the gas and scrubbing liquid in parallel flow with practically no pressure drop on the gas side.

One major problem, when using a scrubber installation, is that the flue gas becomes saturated and the visibility of the plume from the stack increases considerably. This problem is of less importance if the scrubber is used also for hot water generation for the bleach plant. The humidity of the flue gas is then reduced, therefore, reducing the plume. The plume can be virtually eliminated if cold water is available to reduce the humidity ratio still further. (See Figure 10-27.) Cooling of the flue gas adversely affects the plume buoyancy.

10.8 Collection of Particulate Matter from Recovery Boiler Flue Gas

10.8.1 General Conditions

Formation of the particulate matter in the flue gas was explained briefly in 10.2.4. The amount of dust, its particle size distribution, and its handling characteristics depend on the reaction conditions in the recovery boiler.

The dust load varies between 40 and 75 kg per metric ton of dry solids (80 and 150 lb/ton). This gives a range from 140 to 680 kg per metric ton of pulp (280 to 1360 lb/ton) for extreme combinations of operating conditions of recovery boiler operatic . and cooking yield.

The dust concentration in the flue gas calculated on a dry gas basis at standard conditions of 15.5° C and 760 mm Hg (60° F and 29.92 in. Hg) will vary correspondingly from 9 to 25 g/m^3 (4 to 11 gr/dscf). Only the dust that requires high efficiency collection of small size particles is included in these figures. Coarse dust from the sootblowing, which will settle by sedimentation at normal velocities in a settling chamber, is not included since this will be separated in the distribution plenum before the collector elements and will not likely present any burden to the dust collector.

The dust load can increase above the given figures if part of the dry solids is burnt in suspension. The dust from the kraft process consists chiefly of Na_2SO_4 and Na_2CO_3. The concentration of Na_2CO_3 depends mainly on the ratio between sodium and sulfur in the flue gas. Traces of NaCl and Na_2CO_3 are normally found at mills operating with sealogged wood. The concentration of NaCl can be considerable. The concentration of dust in the gas might also be increased by pulping of sealogged wood. The dust particles can contain small amounts of Na_2S.

The present trend of increasing the temperature in the combustion zone to achieve an exit flue gas from the boiler that is virtually free from H_2S and SO_2 also probably increases the dust content in the flue gas, as compared to recovery units of similar, but earlier design. Increases of about 40 percent are possible for a new unit as compared to an old unit at the same mill and operating with the same kind of liquor. The most important data for the design of a dust collector are the gas flow, the dust load, and the particle size distribution. Design data from the recovery boiler manufacturer should be used with appropriate safety margins for the dust collector to cover upset conditions.

The small particle size of the dust makes mechanical dust collectors unsuitable for cleaning of flue gas from recovery boilers. Baghouses are not suitable because of the handling characteristics of the dust. Electrostatic precipitators are, therefore, used for recovery boiler installation. The economic collection efficiency based on the price of the recovered chemicals, capital and operation costs, and payoff time are estimated at between 92 and 97 percent for different conditions. Such a collection efficiency generally will not control particulate emissions to the degree needed to meet air pollution control regulations.

Wet scrubbing of the flue gas with water or with thin black liquor, which was previously oxidized at an efficiency of 99 percent or more and stripped of methyl mercaptans and organic sulfides, can provide sufficient collection efficiency to meet air pollution control regulations. This alternative is, however, less attractive as the chemicals are present in an aqueous solution. The discharge back into the process causes an increase of the inactive chemicals, operational difficulties, and slightly increased losses in other departments. This method may, however, prove the most economical for an old mill under certain conditions.

A combination of an electrostatic precipitator with about 95 percent collection efficiency, followed by a scrubber to achieve a total efficiency of 99.5 percent, is economically favorable if used in combination with heat recovery from the flue gas. The application of a tail end scrubber must be investigated thoroughly for particle size distribution. The collection efficiency is high for dust larger than 1 μm (3.9×10^{-5} in), even with a low energy scrubber (probably because of the hygroscopicity of the dust), but decreases rapidly with decreasing particle size.

10.8.2 Electrostatic Precipitators

The functioning of an electrostatic precipitator is based on movement of charged particles of dust in an electrostatic field. The emission electrodes are given a negative potential ranging from 30,000 to 80,000 volts depending upon operating conditions. They emit electrons that charge the dust particles, and at the same time they form, together with the grounded collecting electrodes, an electrostatic field.

The high tension negative current is achieved with a transformer and a set of rectifiers, normally forming one unit and monitored by a spark rate control unit, designed to give a certain number of flashovers per second. The theory and technology for electrostatic precipitators are comprehensively treated by White (46) and Oglesby (47).

Development work to increase the reliability of the operation and to decrease the capital, operating, and maintenance costs is still in progress. The engineer must consider not only the influence of the gas and dust characteristics, but also the process to which the precipitator has to be applied. The dust and gas characteristics for the recovery boiler process are more favorable for the precipitator operation with the North American recovery boiler system than with the Scandinavian system. This difference is mainly because of higher water vapor content in the flue gas from American direct contact evaporators. This fact should be recognized when new methods for achieving a high black liquor dry solids concentration are considered, or when a change from sootblowing with steam to sootblowing with compressed air is considered.

The negatively charged dust particles move to the grounded collecting electrodes (plates), where they transfer a certain part of their charge, depending on the resistivity of the dust. The dust particles are kept on the plate by the electrostatic field and the remaining charge. The dust is removed from the plates by rapping the plates. The acceleration in the surface of the plates during the rapping must be sufficient to dislodge the dust from the plates by shearing action. The dust falls downwards, mainly following the plates like a web at ideal conditions, and is collected at the bottom of the precipitator. The ideal rapping system should dislodge the whole dust layer with one shock wave passing through the plates. During the shock waves, some flakes of dust that are near the plates retain little charge. These flakes are shaken loose and are very easily entrained in the gas flow. The dust layer should be allowed to build up to a certain thickness between rappings to minimize reentrainment.

The discharge or emitting electrodes collect dust particles with a positive charge and therefore need rapping. The dust collected on the emitting electrodes can vary between needle-like deposits to thick layers of dust if they are evenly distributed. The former type is often found if the dust contains large amounts of chlorides, and the latter if the normal Na_2SO_4-Na_2CO_3 dust is sticky. The acceleration during the shock waves at the rapping usually is about 20-40 times the acceleration due to the earth's gravity (g's) for normal dust. It is very difficult to get an even distribution of the acceleration forces. The acceleration must be increased to above 200 g's if sticky dust is generated at combustion. High stresses are caused above 200 g's on the components of the emitting and collecting system and decrease the periods between major maintenance. These figures relate to parts of the collecting plates where the acceleration is at a minimum. Values considerably higher can normally be measured at the points where the rapping forces are applied.

The dust, collected at the bottom of the precipitator chambers, is discharged in different ways. The dry bottom design used prior to the 1950's in North America was changed to a wet bottom design because of required maintenance of the dry bottom conveyors. The Scandinavian precipitators used dry and wet bottom designs at the start, but changed to mechanical conveyors after experiencing corrosion with the wet bottom design. The difficulties with the conveyors were eliminated by using a heavier steel bolted chain with larger pitch (about 15 cm (6 in)) and bearings of graphite for the shafts to reduce maintenance. Screw conveyors for the transverse transport at the end were changed to Buhler conveyors of the same type as used for cement kilns.

The American trend has been toward dry bottom design with the low odor concept, but the problems associated with heat distribution and heat insulation seem to have been overlooked. The bottom of the precipitator is heated only by the collected dust as the ideal gas velocity below the electric fields is zero. The same conditions are valid for the walls of the precipitator chamber at the sides of the electric fields that are heated only by radiation from the collecting plates nearest the walls. Any gas passing below the fields and at the sides of the fields will decrease the collecting efficiency by "sneakage" and is almost intolerable in high efficiency precipitators.

The collection efficiency is easily calculated assuming an even gas distribution (i.e., the same velocity in all parts of a cross section of the precipitator fields), an even dust distribution in the gas entering the precipitator, and an instantaneous mixing of the gas over the cross section. Deutsch's formula gives the collection efficiency as:

$$\eta = 1 - \exp(-wL/Rc) \qquad \text{Eqn. 10-1}$$

where:

η = the collecting efficiency of the precipitator

w = the overall migration velocity of the dust in m/s (ft/sec),

L = the total effective length of the electric fields in m (ft),

R = the distance between the emitting wire and the collecting plates in m (ft),

c = the gas velocity in m/sec (ft/sec).

Deutsch's formula does not take into account the possible variation in w with the velocity, the possible reentrainment of particles, or the influence of particle size distribution. This formula is valuable to calculate the influence of limited changes (±15 percent) in gas load on precipitator efficiency.

Attempts were made to refine the Deutsch formula to apply it to calculating the difference in performance of particles of different size and therefore evaluate results from test precipitators. Deductions based mainly on results of operation with sodium sulfate, dust from pulverized coal firing, and certain metallurgical processes (48) show that the collecting efficiency is:

$$\eta = 1 - \exp(-\,{}_{w}L/Rc)^{k} \qquad \text{Eqn. 10-2}$$

where the K (dimensionless exponent) normally varies between 0.5 and 0.8.

Equation 10-2 gives less increase in the collection efficiency for a given relative increase in collecting surface than the original Deutsch's formula.

The above formulas can be written in another form that might give a better illustration of the relationship between precipitator size and the gas flow versus the collection efficiency. Observing that the velocity, c, is:

$$c = \frac{G}{AB} \qquad \text{Eqn. 10-3}$$

$$V = A \times B \times L \qquad \text{Eqn. 10-4}$$

where:

G = gas flow, m^3/sec (ft^3/sec)

A = effective height of fields, m (ft)

B = effective width of fields, m (ft)

V = effective volume of electric fields, m^3 (ft^3).

Equations 10-1 and 10-2 can be written as:

$$\eta = 1 - \exp(-wV/RG) \qquad \text{Eqn. 10-5}$$

$$\eta = 1 - \exp(-wV/RG)^{k} \qquad \text{Eqn. 10-6}$$

In addition:

$$B = 2 \times R \times n \qquad \text{Eqn. 10-7}$$

$$C = 2 \times n \times A \times L \qquad \text{Eqn. 10-8}$$

where:

n = number of passages in the field,

n + 1 = number of collecting plates in each field, and

C = total effective collecting plate area, m^2 (ft^2).

Equations 10-5 and 10-6 can be rewritten as:

$$\eta = 1 - \exp(-wC/G) \qquad \text{Eqn. 10-9}$$

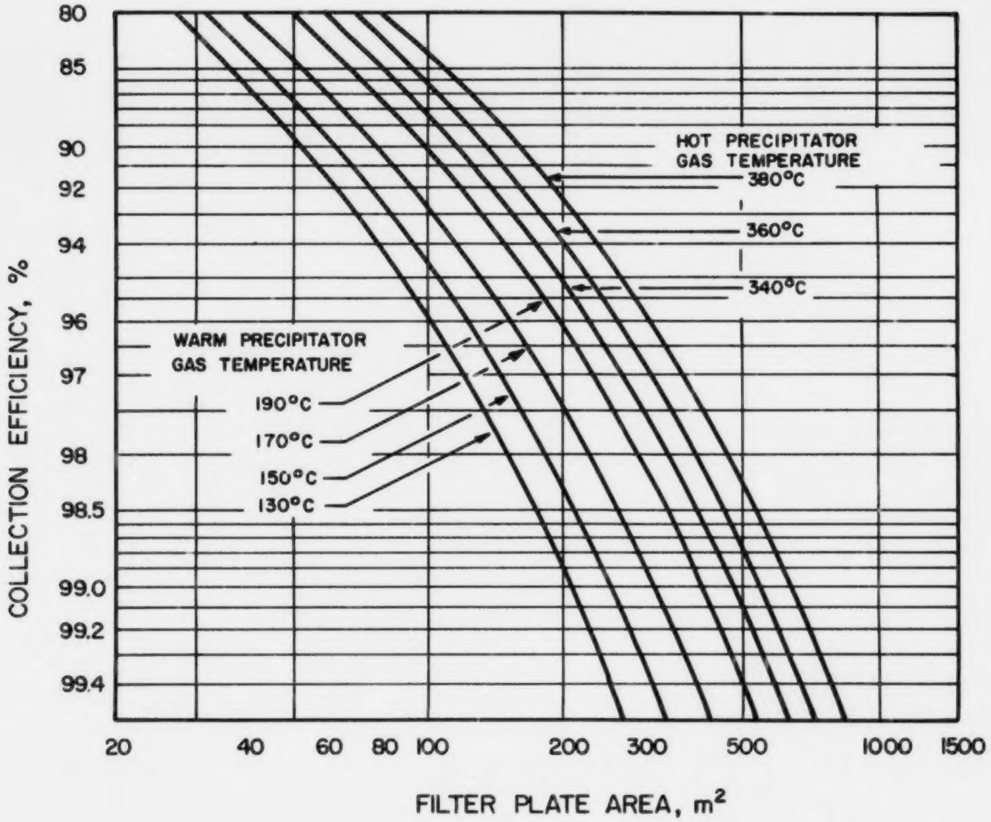
$$\eta = 1 - \exp(-wC/G)^k \qquad \text{Eqn. 10-10}$$

Based on a reasonably large number of tests from precipitators on Scandinavian type recovery boilers, equation 10-10 is recommended for use with $k = 0.7$ for estimating purposes. For American low odor units that have a higher exit flue gas temperature, 205° C or higher as compared to 160° C (400° F vs. 320° F), a value of $k = 0.6$ is recommended. The relative changes in precipitator size with varying collection efficiencies are shown in Figure 10-28.

Comparative tests with different designs of components for electrostatic precipitators must be executed with very accurate control of the flue gas and dust conditions for the tests to be of real value.

The following design parameters are available for the design of electrostatic precipitators. These are:

1. Flue gas flow,
2. Flue gas temperature,
3. Flue gas composition of dry gas,
4. Flue gas moisture content,



CONDITIONS

GAS VOLUME = 5400 m^3/ t D.S.
CO = 16 - 17% by VOLUME
SOLIDS CONC. = 60%

FIGURE 10-28

ELECTROSTATIC PRECIPITATOR SIZE AS A FUNCTION OF COLLECTING EFFICIENCY (37)

5. Flue gas dust content,

6. Particle size distribution of dust,

7. Operating pressure for precipitator,

8. Variations in above data because of temporary overloading, sootblowing, and possible additional gas flows as from dissolving vent stacks, and mix tank vent stacks, and

9. Maximum possible variations because of changes in the pulp production parameters, such as species and pulp yield.

The above list represents more than what was previously available for the design of a precipitator. The demand for accurate information, however, has increased because of the high efficiency currently required. A safety margin above the boiler manufacturer's figures for factors such as gas flow and temperature, should be allowed to accommodate the errors caused by the measurement errors.

The following parameters can be determined for the electrostatic precipitator itself and the regulations for particulate emission. These are:

1. Dust collection efficiency,
2. Number of parallel precipitator chambers,
3. Number of electric fields,
4. Number of transformer-rectifiers,
5. Gas inlet arrangement,
6. Type of rapping and rapping frequencies,
7. Maximum gas velocity in the precipitators,
8. Type of dust discharge, wet or dry bottom,
9. Material of shell for precipitator chambers, and
10. Heating of shell and heat insulation.

The dust collection efficiency must be chosen with some consideration for the degeneration that often takes place in the physical condition of an electrostatic precipitator. The alignment of the emitting electrodes with respect to the collecting plates is important. The alignment is easily upset during the exchange of the high voltage insulators if poor guidance is provided for the adjustment. Because the collection efficiencies can decrease if the alignment is faulty, performance guarantees, over a two-year period from startup, are often requested. Curves for changes in efficiency as function of various parameters, such as gas flow and gas temperature, should be included in the guarantees.

The number of fields and chambers must be determined, taking into consideration the decrease in collection defficiency, if and when one field goes out of operation, causing a subsequent change in outlet dust concentration.

The number of transformer-rectifiers must be determined for possible variations in the specific dust load, temperature, and moisture content at the precipitator inlet. Varying dust loads in different chambers distort the distribution of the current to different chambers if the chambers are coupled in parallel. The more dust in the gas, the lower the voltage and the lower the emission (i.e., the chamber with the highest dust concentration will determine the voltage on all parallel fields). But this chamber will emit less current than the other parallel chamber(s). The efficiency of the fields will, therefore, decrease, especially in the field with the high dust load. This will disturb the next field downstream. The first two fields in each chamber should, therefore, have separate transformer-rectifiers, but coupling the third or later fields in parallel to the same transformer probably is justified if the dust concentration is very low in these fields.

The gas inlet arrangement should allow isolating the precipitator for maintenance, achieving a good gas distribution, and avoiding buildup of dust in the lower part of the inlet plenum, which will eventually disturb the gas distribution. Extension of the bottom conveyor to cover the bottom of the inlet duct is a good solution if sufficient baffling is arranged to avoid sneakage of gas below the fields. Guide vanes and gas distribution plates must be rapped efficiently to give satisfactory performance for a prolonged period.

The rapping mechanisms should be sufficient to clean the emitting electrodes and collecting plates without being actuated for extended periods. The main part of the dust layer probably is discharged in the beginning of the rapping and extended rapping tends to break away flakes of dust, causing "snowflaking." Tests show large increases in dust losses with increases above the optimum frequency of rappings.

The gas velocity in an electrostatic precipitator must be limited to avoid snowflaking. A velocity not exceeding 1.0 m/s (3.5 ft/sec) is recommended for American design (47). This normally is the practice also for Scandinavian precipitators, except where the precipitator is followed by a scrubber for heat recovery, in which case higher velocities are acceptable.

The dust discharge can be accomplished with black liquor pumped over the bottom either continuously or intermittently. Some designs use impellers in the bottom to stir the dust into the black liquor. The black liquor is then discharged to the cascade evaporator or to a mixing tank. The gas velocity between the baffles that prevent sneakage of gas below the electric fields is very low. Here the gas acts, to some extent, as a revolving gas volume at approximately the wet bulb temperature. Corrosive conditions are easily reached in the lower part of the fields, especially if the black liquor contains a high concentration of chlorides. Such conditions adversely affect the lifetime of the emitting electrodes and, in some cases, have also damaged the lower parts of the collecting plates.

Using a dry bottom avoids these difficulties, but proper chains and scrapers with sufficient strength and stability must be provided. The transverse conveyor, preferably at the inlet end of the precipitator, should have sufficient capacity to accommodate the uneven feeding from the different fields. Drag chain conveyors of the same type as normally used for cement kilns, give outstanding service. If screw conveyors are used, they must have a relatively large diameter and sufficient stiffness to avoid vibrations. The troughs for the transverse conveyor should not have more depth than is the necessary minimum.

The reason for minimizing the depth is to keep the temperature high and avoid condensation of water vapor into the hygroscopic dust. The troughs must be well insulated. The dust is preferably discharged via a rotary valve to seal against air leakage into the precipitator chamber. (The induced draft fan operates better if it is placed on the clean side of the precipitator.) Air leakage can cause local corrosion, which can disturb the gas distribution.

The rotary valve should be isolated from the mixing tank by a short screw conveyor with an air screen to prevent diffusion of water vapor up into the rotary valve and the dust conveyor. This arrangement has proved reliable in avoiding plug-ups of the rotary valve and dust conveyors. The necessary amount of air for the air screen is less than 1.7 m^3/min (60 ft^3/min) per precipitator chamber, and this air normally passes out through the vent on the mixing tank.

The normal precipitator housing in North America consists of tile walls and concrete roof and little heat insulation. This design is susceptible to cracking with subsequent air leaks and inside corrosion. The concrete housing used in Scandinavia was designed to avoid cracks by proper consideration of heat conduction. This design was used as long as the gilled cast iron economizer was still in use. The precipitator must be water washed at intervals of a few days to two weeks. The temperature of the flue gas to the precipitator can be as low as 110° C (230° F) for about one work shift immediately following a water washing. Hot precipitators with steel plate chambers placed between the boiler outlet and the economizer that operated at 400° C (750° F) or slightly lower, came into use in 1957. This design was adopted for use with the current long vertical tube economizer. The exit flue gas temperature is around 160° C (320° F). Experience seems to indicate that a steel plate shell can be used down to 127° C (260° F) if the precipitator is equipped with very good heat insulation of at least 10 cm (4 in) of mineral wool above the top of the stiffeners for the shell. All stiffeners and flanges in ducts must be insulated.

Heating of the shell is probably not necessary if good heat insulation is supplied. Heating of precipitators was standard practice before starting of the operation in Scandinavia, but has now been abandoned. No corrosion damage has been observed, to date. The present practice in the U.S.A. and Canada of not covering the stiffeners with sufficient insulation is, however, damaging, and if it is economically feasible to use a heated chamber instead of good insulation, the method should be used.

Dust emission data from recovery boiler electrostatic precipitators used presently in the U.S.A. are given in Table 10-10. The values are average values of decile groups. The table includes information from precipitators on 87 recovery boilers.

TABLE 10-10
AVERAGE PARTICULATE EMISSIONS FROM RECOVERY BOILER ELECTROSTATIC PRECIPITATORS IN THE UNITED STATES (49)

Emission decile	Average Emission rate	
	kg/t	lb/ton
First (lowest)	1.1	2.1
Second	1.7	3.3
Third	2.4	4.8
Fourth	3.4	6.8
Fifth	6.2	12.4
Sixth	8.5	17.0
Seventh	9.2	18.4
Eighth	14.2	28.4
Ninth	23.2	46.3
Tenth (highest)	37.6	75.2

The first decile represents dust concentration of 0.11 g/m^3 (0.05 gr/dscf), the fifth 0.46 g/m^3 (0.2 gr/dscf), and the tenth 2.3 g/m^3 (1 gr/dscf). The collection efficiencies are 99 percent, 95 percent, and 80-90 percent, respectively.

10.8.3 Liquor Scrubbing of Recovery Boiler Flue Gas

The cyclone evaporator and the venturi evaporator scrubber were originally used for the recovery of heat and for concentration of the black liquor to a level suitable for firing in the furnace. The cyclone evaporator was a low energy type of scrubber that collected only the coarsest size fractions of the dust in the flue gas. The venturi evaporator scrubber has high energy requirements but is capable of collecting finer dust than the cyclone evaporator. The dust collecting efficiency was decreased by the high viscosity of the concentrated black liquor used in these types of scrubbers. This liquor cannot be atomized into sufficiently small drops for efficient dust collection. The capital cost for the recovery boiler department was considerably decreased by the introduction of the venturi evaporator scrubber, as the venturi scrubber and its associated enlarged induced fan compared favorably with alternative types of heat recovery equipment with a low efficiency electrostatic precipitator. The operating costs were probably never favorable because of high power consumption and rather large losses of Na_2SO_4. A combination of high interest rate for the capital and a low price for electric power can, however, sometimes justify the choice of the venturi evaporator scrubber, if air pollution control is not an overriding factor. These types of scrubbers were discussed previously in section 10.6.

To achieve high collection efficiencies for the particulate matter in the flue gas, liquors with low viscosity must be used, such as thin black liquor or water. A scrubber using thin black liquor discharges its liquor with the dissolved dust to a multiple-effect evaporation plant. The increased load of Na_2SO_4 and/or Na_2CO_3 in the black liquor charged to the evaporation plant increases the fouling rate. A comparison between a scrubber using thin black liquor and a precipitator should, therefore, consider the changes needed in the evaporation plant. Such changes include increasing the heating surfaces to compensate for the increased fouling rate and to accommodate the increased boiling point rise. Another factor to consider is the cleaning of the evaporation plant by boiling out with water and its attendant disturbances in the operation. Oxidized liquor must be used to avoid emission of H_2S, and so allowance must be made for the corresponding heat loss from oxidation.

Water can be used in the scrubber; the dust is then collected and discharged as a water solution. This solution cannot be concentrated very much before crystallization occurs. The recovery of the chemicals will, therefore, have an influence on the evaporation plant of the same magnitude as when black liquor is used as the scrubbing liquid. The emission of H_2S, however, is avoided if the dust is reasonably free from Na_2S.

Existing precipitators which were designed for insufficient collection efficiency to meet the present regulations for emission of particulate matter, or which have degenerated to a lower collection efficiency because of design deficiencies and/or inadequate maintenance, can be retrofitted with scrubbers. The dust amount collected in these scrubbers is reasonably small. and influence on the recovery cycle is less than if the scrubber installation were to collect the total dust load of the flue gas.

Using flue gas scrubbers in many cases provides an attractive solution to increasing the total collecting efficiency of an existing recovery boiler plant. But the space requirement for an additional precipitator may make it almost impossible to use an additional precipitator. Operational problems can very likely occur if long horizontal ducts are used to convey the gases from an existing plant to an additional electrostatic precipitator. Using a flue gas scrubber can then provide a practical solution that also results in a capital cost saving. A venturi type of scrubber is used in most such cases but it has a relatively low pressure drop of 1500-2500 Pa (6-10 in. w.g.).

Another solution was practiced in a number of mills in cold climates. A low energy type flue gas scrubber can be used for recovery of heat from the recovery boiler flue gas to produce hot water for the bleaching plant (and possibly also for the brown stock washing). A scrubber of this type is placed after the electrostatic precipitator to collect some of the remaining dust from the flue gas. Combinations of electrostatic precipitators of 95 percent, or even lower, collecting efficiency with a scrubber, recovering heat for producing hot water, have given a combined collection efficiency of 99.5 percent and have operated successfully for several years (41, 50). This is a very economical combination, as the cost of the scrubbers is justified by both heat recovery for heating water and saving in the cost of a smaller precipitator. Mills in warm or hot climates where hot water is usually available in abundance cannot use this approach effectively. The decrease in the generation of back pressure power is an important factor in an economic evaluation, because it can reduce the value of the saving in fuel by up to 50 percent.

Use of scrubbers in existing mills to increase the total collection efficiency of the existing precipitators should be carefully evaluated. The particle size distribution after the precipitators is important to the collecting efficiency of the scrubber. The collection efficiency declines rapidly with decreasing particle size. The same precipitator design can have great variations in amounts of fine dust at the exit at operating conditions which seem very similar when based on the data for the electric current and voltage in the precipitator fields. Therefore, new equipment should be guaranteed by the supplier covering both the efficiencies of the precipitator and the scrubber.

The efficiency of the scrubbing depends mainly on the contact surface area and relative velocity between the water drops and the dust particles. The atomization of the liquid and the relative velocity between the gas and the liquor drops can be achieved in either or both of two ways, acceleration of the gas and applying the liquor through high pressure atomization nozzles. Pressures up to 10.3 MPa (1,500 psig) are sometimes used for the atomization of water. Similar drop size is achieved by using steam or compressed air with a pressure of about 0.79 MPa (100 psig). Atomizing by accelerating the gas to high velocities can avoid clogging of the nozzles if the liquid is recirculated. Atomization of the liquid by using gas velocity consumes much more power than atomization by high pressure nozzles. One particularly interesting design is the use of co-current water sprays. The impact from the water drops will reduce the pressure drop in the venturi throat, and designs are available in which the impact from the water drops compensates for the pressure drop of the gas in the scrubber (45).

10.9 Economy of Recovery Boiler Operation

Recovery of the chemicals and heat from the black liquor dry solids is of vital importance to the economics of pulp production. The great variations in climatic conditions and in pulp yields for different species of wood make it very difficult to give a general picture. The prices for electric power also vary considerably and, consequently, affect the economic feasibility of back pressure power generation. Power generation favors feed water heating with steam from the turbine extractions. The correspondingly higher feed water temperature might make changes necessary in the arrangement of the economizer and air heater and in the most economic exit gas temperature.

The changes in the design and operation of recovery boilers, as a result of the last few years' accumulation of research data, might make them more economical. Diagrams for the capital cost for recovery boilers, for electrostatic precipitators, and for the complete recovery boiler department are given in Figure 10-29. The price level is for January 1974. The price for the boiler is given for steam conditions of 4.2 MPa (600 psig), 400° C (750° F) for low back-pressure power generation and 8.4 MPa (1,200 psig) and 480° C (900° F) for reasonably high back-pressure power generation.

Two flue gas temperatures, 160° C (320° F) and 250° C (480° F), were stated for the prices for electrostatic precipitators. The lower price for the precipitator at 160° C (320° F) must be compared with an increase in price for an air heater-economizer. The handling characteristics of the dust are, however, much better at the lower temperature.

Rather high exit gas temperatures were used in the U.S.A. and Canada as compared to Scandinavia. They reflect the low fuel prices in North America. Figure 10-30 shows the heat loss per °F per year in the exit gas for varying firing rates. The value of the heat loss per year for the difference in exit flue gas temperature between American and Scandinavian practice is shown for varying fuel prices in cost per million BTU of steam.

Price Level Jan. 1974

"Average Black Liquor Dry Solids"

A. Recovery Boiler, delivery & erection, 400°F exit gas. Low odor with economizer.

B. Electrostatic Precipitator, collecting efficiency, 99.5%

C. Complete R.B. Department, including building ventilation, instrumentation, electric power supply, feed water treatment, black & green liquor systems connected to mill, steam lines to back pressure turbine, stack, & dissolving vent stack condensor.

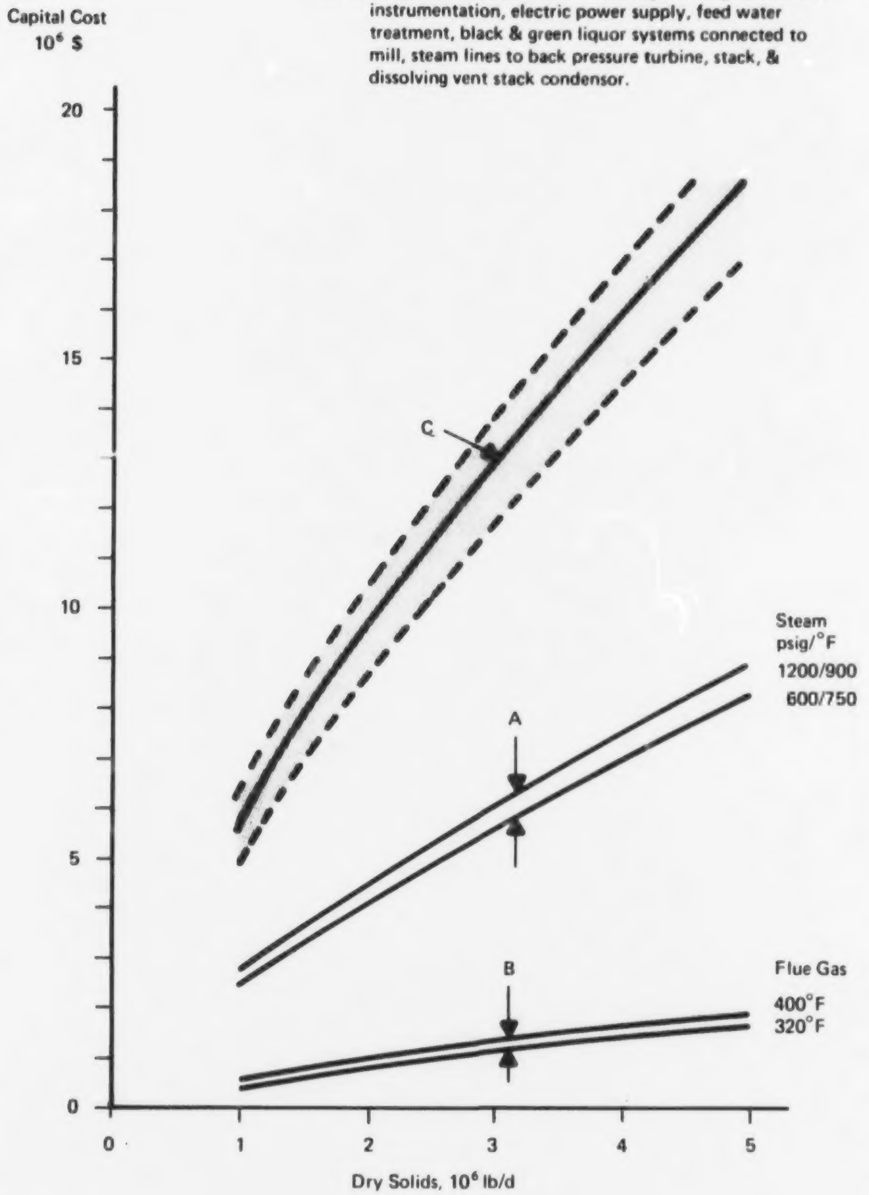
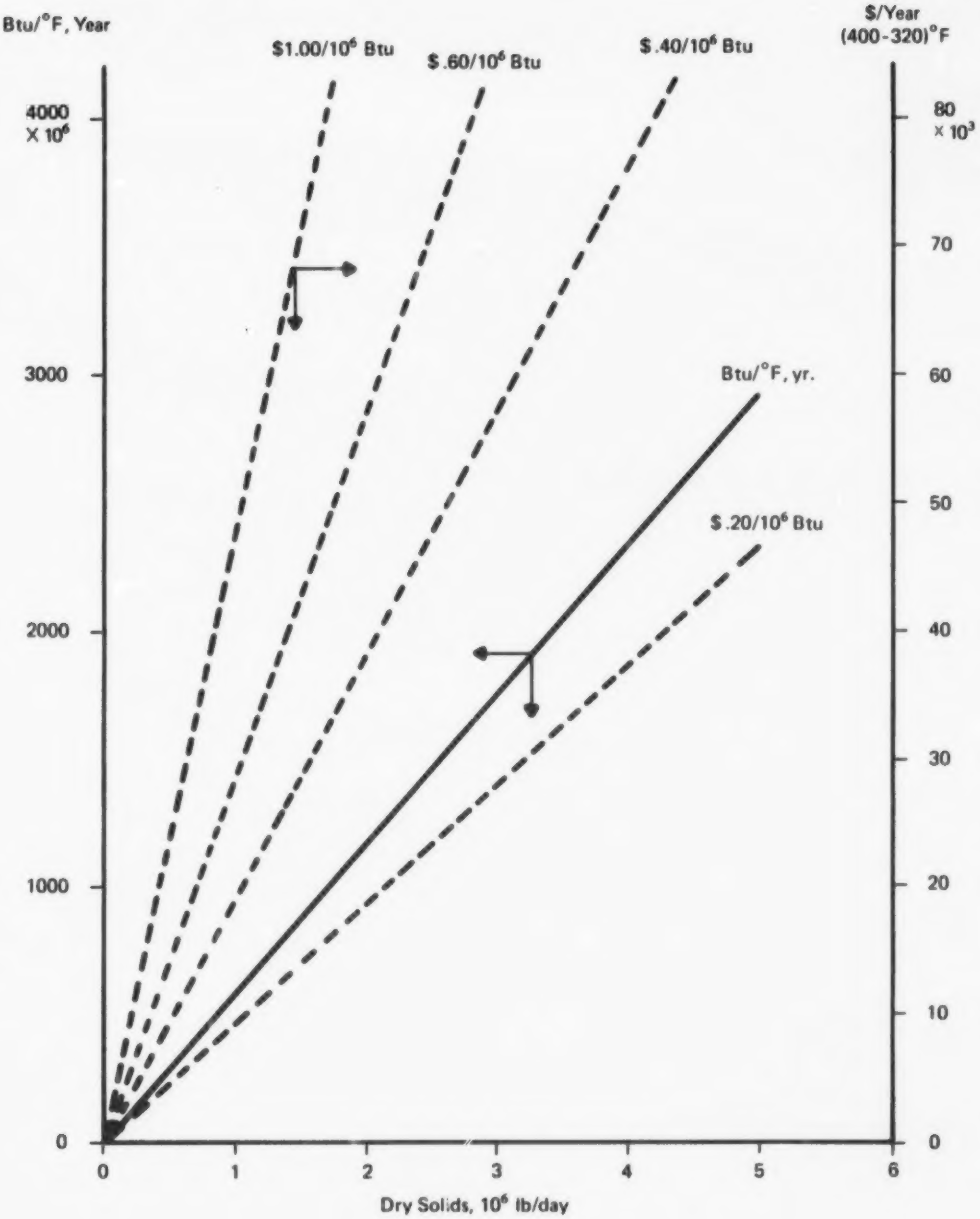


FIGURE 10-29

CAPITAL COST FOR RECOVERY BOILER DEPARTMENT



"Average Black Liquor Solids"
Black liquor concentration 62%, excess air, O_2 at exit, 400-320°F represents exit flue gas temperatures according to the American & Swedish design practice respectively.

FIGURE 10-30
FLUE GAS ENERGY LOSSES

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APPENDIX 10-1: AIR AND FLUE GAS QUANTITIES AT COMBUSTION OF BLACK LIQUOR DRY SOLIDS

NOTE: Neither vapor from the water in the black liquor or air from sootblowing has been included. No air leakages have been considered.

Assume:
Reduction of smelt is 100 R%
No formation of Na_2S_n or $Na_2S_2O_3$
Dust losses after precipitator negligible.
Dry Air is $\frac{1}{4.77}$ parts O_2 and $1 - \frac{1}{4.77}$ "N_2" (includes CO_2, argon, etc.)
Humidity ratio of air is w lb/lb dry air
Volume ratio of moist air/dry air $m = 1 + \frac{29}{18} w$
Black liquor D.S. composition is:

carbon, C	100 c%
hydrogen, H	100 h%
sodium, Na	100 n%
sulfur, S	100 s%
oxygen, O (as difference)	100 o%
inert oxides	100 i%

$c + h + n + s + o + i = 1$

Theoretical complete combustion without excess air

Product	Quantity moles/lb D.S.	Air, moles/lb D.S.		Flue gas, moles/lb D.S.			
		O_2	Air	CO_2	H_2O	N_2	Total
CO_2	$\frac{c}{12} - e = a$	a	4.77 ma	a	4.77 (m − 1) a	3.77 a	4.77 ma
H_2O	$\frac{h}{2.016} = b$	0.5 b	0.5 × 4.77 mb	–	[1 + 0.5 × 4.77 (m − 1)]b	0.5 × 3.77 b	0.5 b + 0.5 × 4.77 mb
Na_2S	$R \frac{s}{32.07}$	–	–	–	–	–	–
Na_2SO_4	$(1 - R) \frac{s}{32.07} = d$	2 d	2 × 4.77 md	–	2 × 4.77 (m − 1) d	2 × 3.77 × d	2(4.77 m − 1) d
Na_2CO_3	$\frac{n}{45.98} - \frac{s}{32.07} = e$	1.5 e	1.5 × 4.77 me	–	1.5 × 4.77 (m − 1) e	1.5 × 3.77 × e	1.5 (4.77 m − 1) e
Corr. for O_2	$\frac{o}{32} = f$	−f	−4.77 mf	–	−4.77 (m − 1) f	−3.77 f	− (4.77 m − 1) f

At theoretical complete combustion without excess air

Air consumption, $A = 4.77\ m\ (a + 0.5b + 2d + 1.5e - f)$ moles/lb D.S.
Dry flue gas flow, $F_{dry} = 4.77\ a + 3.77\ (0.5b + 2d + 1.5e - f)$ moles/lb D.S.
Total flue gas flow, $F_{tot} = 4.77\ m\ (a + 0.5b + 2d + 1.5e - f) + 0.5b - 2d - 1.5e + f$ moles/lb D.S.
Water vapor, $F_v = 4.77\ (m - 1)\ (a + 0.5b + 2d + 1.5e - f) + b$ moles/lb D.S.

$$\%\ CO_2\ \max = \frac{100\ a}{4.77\ a + 3.77\ (0.5b + 2d + 1.5e - f)}\ \%$$

The flue gas flow F_z, at z% by volume oxygen in dry gas is $F_z = F_{dry} \left[1 + \frac{\frac{z}{100}}{4.77} - z \right] + F_v$

APPENDIX 10-2. HEAT VALUES VS. OXYGEN DEMAND FOR COMPLETE COMBUSTION

Variable	Units	Softwood Lignin	Hardwood Lignin	Carbo-hydrates
Analysis		A	B	C
Carbon, C	%	64	60	46
Hydrogen, H	%	6	6	6
Oxygen, O	%	30	34	48
Bomb heat value (X)	Btu/lb	11340	10620	7560
Oxygen demand for complete combustion	10^{-3} lbmole/lb	58.8	54.3	38.2
Analysis adjusted to "normal" content of inorganics		A_1	B_1	C_1
Carbon, C	%	47.8	44.8	34.6
Hydrogen, H	%	4.4	4.4	4.4
Oxygen, O	%	25.6	28.6	38.8
Sodium, Na	%	18.2	18.2	18.2
Sulfur, S	%	4.0	4.0	4.0
Bomb heat value (0.734 X)	Btu/lb	8300	7800	5550
"Efficient heat value in reducing atmosphere" (reduction for sulfide, and heat of evaporation for vapor from combustion of hydrogen)	Btu/lb	7340	6840	5890
"Resulting heat value of black liquor" (above value adjusted for heat of evaporation of water in black liquor)	Btu/lb	6390	5890	3640
Oxygen demand for complete combustion	10^{-3} lbmole/lb	44.2	40.8	29.1

Note: See Figure 10-23 regarding linear correlation.

CHAPTER 11

LIME BURNING AND LIME DUST HANDLING

The causticizing of liquor, commonly called green liquor, from the smelt dissolving tank by addition of lime or calcium oxide (CaO) results in the generation of a lime mud or calcium carbonate ($CaCO_3$) sludge. The lime and sludge are then washed and calcined at elevated temperatures in either a rotary kiln or a fluidized bed calciner to recover calcium oxide. This oxide can then be reused for reclaiming additional white liquor, the chemical solution for digesting pulp. The normal auxiliary fuels used as heat sources for lime mud burning are natural gas and residual fuel oil. The two major potential air pollutants from lime mud burning are the gaseous emissions and the particulate emissions of entrained lime dust from the burning zone. The gaseous emissions are H_2S from the lime mud and, possibly, organic sulfur compounds from the scrubbing water.

11.1 Rotary Lime Kilns

11.1.1 Design Features

The rotary kiln is the most commonly employed device for lime mud reburning in kraft pulp mills. The device is an open-ended inclined cylinder that is rotated so that lime mud added at the upper end gradually passes to the lower end and drops out into a bin as dry lime. Fuel and air flow countercurrently to the lime from the lower end of the kiln. The kiln exhaust gases normally pass through a mechanical cyclone collector for lime dust recovery and finally through a liquid scrubber for particulate control (1).

Rotary lime kilns employed in kraft pulp mills can range from about 2.4 to 4.0 m (8 to 13 ft) in diameter and from about 30 to 120 m (100 to 400 ft) in length. They are designed to burn 36 to 360 t (40 to 400 tons) of lime (as dry CaO) per day (2). The lime kilns are normally inclined at a slope of about ten degrees from the horizontal plane and can be supported by two- to four-supports, depending on their length. The lime kilns must be designed with a number of auxiliary components, including a lime mud feed system, hot lime conveying system, air inlet and preheating system, gas exhaust system, kiln rotation system, and instrumentation systems (3). Major kiln design variables include kiln length, kiln diameter, rotation speed and angle of incline, which influence solids retention time, gas-solids contact area, and temperature.

11.1.2 Operating Parameters

Lime mud at 55 to 65 percent solids and with sodium content of 0.1 to 2.5 percent by weight (as Na_2O) enters at the upper end of the lime kiln and passes through successive stages of water evaporation, mud preheating, and lime calcination. Temperatures in the kiln vary from 150 to 260° C (300 to 500° F), at the upper or wet end, to 1200 to 1300° C (2200 to 2400° F) at the hottest part of the calcination zone near the lower or dry end. Energy requirements for the lime kiln operation are for water evaporation, preheating and calcining the lime mud, and power to rotate the lime kiln, drive the air fans and flue gas fans, pump the scrubber liquid, and convey the lime mud and reburned lime. The major types of fuels burned in lime kilns are natural gas and residual fuel oil; turpentine and coal may also be used. Fuel requirements for lime kilns and fluidized bed calciners are listed in Table 11-1.

Two of the major design variables affecting particulate emissions from lime kilns are kiln length and diameter. These variables can affect the amount of particles swept from the kiln exhaust gases by governing the gas velocity and the gas-solids contact area.

TABLE 11-1
ENERGY REQUIREMENTS FOR LIME MUD CALCINING
SYSTEMS (3) (4)

Rotary Kiln		Fluid Bed Calciner	
kJ/t	(BTU/ton)	kJ/t	(BTU/ton)
$2.3\text{-}4.7 \times 10^6$*	$(2\text{-}4 \times 10^6)$*	$2.1\text{-}2.5 \times 10^6$	$(1.8\text{-}2.0 \times 10^6)$*
$9.3\text{-}17.4 \times 10^6$**	$(8\text{-}15 \times 10^6)$**	$8.0\text{-}9.2 \times 10^6$	$(7\text{-}8 \times 10^6)$**

*per metric (t) or short ton (ton) of pulp.
**per metric (t) or short ton (ton) of lime, as CaO.

H_2S emissions from the lime kiln are affected by the Na_2S content of the lime mud (particularly the aqueous phase) and by the presence of Na_2S in the scrubber wash water. The use of digester and evaporator condensate as lime kiln scrubber water can result in the stripping of organic sulfur compounds into the exit flue gas. The presence of sufficient excess air in the kiln can reduce the concentration of H_2S in the exhaust by providing an oxiding atmosphere sufficient for H_2S conversion to SO_2 (5).

11.2 Fluidized Bed Calciners

Fluidized bed calciners are alternatives to rotary lime kilns for the calcination of lime mud to lime. The lime mud is first washed to reduce soluble sodium compounds to a sodium content of 0.1 to 0.5 percent by weight (as Na_2O) and then dried on a vacuum filter. The dried lime mud at 55 to 65 percent solids is then suspended in the flue gas from the fluidized beds at a temperature of about 150° C (300° F) to evaporate the water. The solids are then passed through a two-stage cyclone system to recover the dried lime mud solids and then fed into a bed of fluidized lime pellets formed by calcination. The bed is kept in suspension by the action of an air fan located below the cooling chamber from which reburned lime is removed. Natural gas or fuel oil is injected into the suspended bed and burned to provide the heat necessary for the calcination reactions to take place at a temperature of about 825 to 875° C (1500 to 1600° F). The entrained particles and the combustion gas products then pass out from the calciner to entrain the wet mud and pass through the two-stage cyclone system and a venturi scrubber for particulate removal (5).

Fluidized bed calciners are employed at several kraft pulp mills and have lime burning rates ranging from 23 to 136 t per day as CaO (25-150 ton/day). Fuel requirements for fluidized bed calciners are generally lower than for lime kilns because of the small combustion chambers used which have smaller radiation heat losses. Electricity requirements for fluidized bed calciners, however, are generally greater than for rotary kilns because of the energy required for suspending the bed and operating the venturi scrubber. Major operating variables affecting fluidized bed reactor operation are the mud drying temperature, the calcination zone temperature, the excess air level, the bed fluidization level, and the sodium content of the lime mud.

Major operating variables affecting particulate emissions from the calciner unit are the air sweep velocity and the lime feed rate. Variables affecting gaseous emissions from fluidized bed calciners are the same as those affecting reduced sulfur emissions from rotary lime kilns.

11.3 Particulate Emission Control

The major means of controlling particulate emissions from lime kiln and fluidized bed calciner exhaust gases are liquid scrubbing, using either an impingement or venturi-type scrubber, and, recently, electrostatic precipitation. The scrubbing devices are usually placed following a mechanical cyclone collector used either for removal of the larger lime dust particles, as with lime kilns, or for predrying the lime mud for fluidized bed calciners. Particulate inlet loadings to scrubbing devices from lime kilns can range from 7 to 35 g/m^3 (3 to 15 gr/cu ft) at standard conditions of 21.1° C, 1.0 atmosphere, dry gas (70° F, 29.92 in. Hg, dry gas). The dust losses constitute about 1 to 5 percent of the total dry solids load to the kiln. Particle size measurements for the above mass concentrations are not reported with these data, but the lime particles generally comprise the larger sizes and sodium particles the smaller ones (4). Comparable data are not available for fluidized bed calciners, but it is necessary to use a two-stage cyclone mud drying system to avoid overloading the venturi scrubber.

11.3.1 Scrubbing Systems

The major types of scrubbers employed on lime kilns, to date, are the impingement and venturi types, with cyclonic scrubbers also employed, but to less extent. Impingement type scrubbers were extensively employed in the past for particulate scrubbing on lime kilns and have the advantages of relatively low pressure drop and scrubber shower rate, with resultant reduced operating costs. The devices are limited, however, in their maximum scrubber slurry water solids concentrations due to possible scrubber plugging. In addition, they normally have lower particulate removal efficiencies because of less efficient gas-liquid contact. Impingement type scrubbers have higher capital costs than venturi scrubbers on similar installations basically due to their larger size and greater complexity.

Venturi scrubbers are commonly used on lime kilns at the newer kraft pulp mill installations primarily because of higher particulate removal efficiencies than achievable by the older impingement type scrubbers. Venturi scrubbing systems can operate with slurry water solids concentrations of up to 30 percent by weight without excessive plugging. A summary of operating characteristics for kraft lime-kiln scrubbers is presented in Table 11-2 (4).

TABLE 11-2
OPERATING CHARACTERISTICS FOR PARTICULATE LIQUID SCRUBBERS EMPLOYED ON KRAFT LIME KILNS (4)

Parameter	Scrubber Type Impingement	Venturi
Shower rate ratio, l/m^3	0.54-2.0	1.73-3.21
($gal/10^3\ ft^3$)	(4-15)	(13-24)
Slurry solids, % by wt.	1-2	10-30
Pressure drop, mm Hg	9-13	19-28
(in H_2O)	(5-7)	(10-15)
Power required,* kW per t/day	0.041-0.049	0.082-0.099
(hp per ton/day)	(0.05-0.06)	(0.10-0.12)
Power required,** kW per t/day	0.13-0.16	0.27-0.34
(hp per ton/day)	(0.16-0.20)	(0.33-0.42)

*per mass of pulp.
**per mass of lime.

11.3.2 Performance Characteristics

A number of studies were conducted to determine particulate collection efficiencies of lime kiln scrubbers. Stuart and Bailey (6) report that venturi scrubbers were able to achieve 96-97 percent particulate removal from lime kiln exhaust gases at pressure drops of 1.7 to 2.8 kPa (7 to 10 in water); while Landry and Longwell (7) report that venturi scrubbers can achieve particulate removal efficiencies of 98-99 percent at pressure drops of 2.4 to 3.7 kPa (10 to 15 in water). A series of studies were conducted on a joint basis by the National Council for Air and Stream Improvement and the U.S. Environmental Protection Agency to establish the particulate collection efficiencies of 66 existing lime kiln scrubbers. Venturi scrubbers were able to produce consistently higher particulate collection efficiencies than the impingement scrubbers, as shown in Table 11-3 (2).

TABLE 11-3
PARTICULATE COLLECTION EFFICIENCIES FOR LIQUID SCRUBBERS ON KRAFT PULP MILL LIME KILNS (2)

	Impingement Scrubbers		Venturi Scrubbers	
Parameter	Average	Range	Average	Range
Inlet concentration,* g/m^3	27.38	8.00-33.96	18.60	5.85-31.83
(gr/cu ft)	(11.94)	(3.50-14.81)	8.11	(2.55-13.88)
Outlet concentration,* g/m^3	1.78	0.99-3.56	0.73	0.27-2.29
(gr/cu ft)	(0.78)	(0.43-1.56)	(0.32)	(0.12-1.00)
Removal efficiency, % by wt.	92.2	86.8-96.9	94.8	85.5-99.1
Emission rate,** kg/t	1.78	1.14-2.09	1.01	0.33-2.60
(or lb/ton)	(3.55)	(2.28-4.18)	(2.02)	(0.66-5.19)

*Concentrations are reported at standard conditions of 21.1° C and 760 mm Hg (70° F and 29.92 in Hg), dry gas.

**Emission rates are based on an air-dried ton of pulp basis (i.e., 10% moisture, by weight).

Information developed during the study indicates that high pressure drop venturi scrubbers can achieve significantly lower particulate levels than reported in Table 11-3 (2). Particulate concentrations at standard conditions of between 0.02 and 0.11 g/m^3 (0.01 to 0.05 gr/cu ft), corresponding to emission rates of 0.01 to 0.05 kg per air dried metric ton of pulp (0.02 to 0.1 lb/ton), were measured. Very little information exists regarding particulate emission control following fluidized bed calciners. Erdman (8) reports on a high pressure drop venturi scrubber following a two-stage cyclonic mud drying system. The pressure drop through the venturi is 5.4 kPa (22 in water). Although the dust carryover from the calciner section is 12 percent, the scrubber emits a particulate concentration of 0.16 g/m^3 (0.07 gr/cu ft), which corresponds to an emission rate of 0.24 kg per metric ton of pulp (0.49 lb/ton).

11.4 Gaseous Emission Control

Lime mud calcining in rotary kilns or fluidized bed reactors can emit H_2S, organic sulfur, SO_2, and nitrogen oxides to the atmosphere. The gaseous emissions result either from materials entering the calcining unit system or from materials entering the kiln. The major process operating variables affecting gaseous emissions include excess air level, operating temperature, and solid and gas-phase retention times.

Major input material properties affecting gaseous emissions include the respective Na_2S contents of the input lime mud and scrubber water, organic sulfur levels in the inlet scrubber water, and the moisture content of the lime mud. The major design variable affecting gaseous emissions from the calcining system are the length and, to a lesser extent, the diameter for rotary kilns, and the diameter and height for fluidized bed calciners.

A summary of gaseous emissions from rotary lime kilns and fluidized bed calciners is presented in Table 11-4.

TABLE 11-4
GASEOUS EMISSIONS FROM KRAFT PULP MILL LIME KILNS (2)

Gaseous Constituent	Concentration Average	Concentration Range	Emission Rate Average	Emission Rate Range
	ppm, by volume		kg sulfur per t pulp (lb sulfur per ton pulp)	
H_2S	108	0-500	0.24 (0.48)	0-1.88 (0-3.76)
CH_3SH	14	0-90	0.03 (0.07)	0-0.17 (0-0.34)
CH_3SCH_3	27	0-245	0.02 (0.05)	0-0.22 (0-0.43)
CH_3SSCH_3	5	0-11	0.01 (0.03)	0-0.10 (0-0.20)
TRS	–	–	0.31 (0.63)	0-2.37 (0-4.73)
SO_2	34	0-140	0.14 (0.28)	0-1.11 (0-2.20)

11.4.1 Lime Mud

The most important gaseous emissions from lime reburning systems are malodorous reduced sulfur compounds. Hydrogen sulfide can be volatilized from the Na_2S present in the lime mud by contact with CO_2 from the flue gas. Above a threshold Na_2S concentration of 0.2 percent by weight, the generation of H_2S is directly proportional to the residual Na_2S content of the lime mud. This linear relationship is similar to that for direct contact evaporation (9). The amount of H_2S released can be controlled by reducing the residual Na_2S level by more efficient lime mud washing. It is not normally feasible, however, to reduce the residual sodium content in the lime mud to less than 0.1 percent by weight because of possible mud ring formation.

Prakash and Murray (5) report that H_2S emissions from the lime mud occur primarily from Na_2S dissolved in the aqueous portion and not from the solid portion of the lime mud. The H_2S emissions can be reduced by drying the mud to a solids concentration of 70 percent by weight or more before burning.

11.4.2 Scrubbing Water

The scrubber water can be a source of both H_2S and organic sulfur compounds emissions from kraft mill calcining units equipped with scrubbers. The presence of Na_2S in the scrubber water can result in the release of H_2S by contact with CO_2 if the liquid pH is sufficiently low. The emission rate of H_2S and organic sulfur compounds increases with the inlet Na_2S and organic sulfur concentrations, with rising liquid- and gas-phase temperatures, and with an increasing degree of gas-liquid contact, as represented by the scrubber pressure drop. The potential for organic sulfur release is particularly great if untreated digester or evaporator condensates are used as lime kiln scrubber makeup water.

Caron (11) reports that using lime mud wash water instead of fresh water for lime kiln scrubbing results in stripping of 0.10 to 0.22 kg sulfur per metric ton of pulp (0.2 to 0.4 lb sulfur/ton) as compared to an absorption of only 0.035 kg sulfur per metric ton of pulp (0.07 lb sulfur/ton) with fresh water. Normally, fresh water should be employed as the scrubbing medium to avoid the stripping of odorous gases. If condensate waters are employed, steam stripping should be employed prior to the scrubbing operation.

One U.S. mill has significantly reduced TRS emissions from a lime kiln venturi scrubber by adding sodium hydroxide to the scrubber water to raise the pH. The scrubber water is recycled to the causticizing system (10).

11.4.3 Combustion Variables

The major combustion variables that can affect reduced sulfur emissions from lime mud calcining operations are the excess air level, the temperature profile, and the mud retention time in the kiln. Caron (11) reports that the TRS emissions from the combustion zone are minimized at excess oxygen levels of four percent by volume or greater. Though no definite patterns have been established, the kilns that have cooler wet-end temperatures tend to have relatively higher reduced sulfur emissions because the sulfur compounds can be volatilized without burning. Sufficient retention time must be provided at temperatures above 760° C (1400° F) to oxidize the reduced sulfur compounds.

Walther and Amberg (12) report that shorter lime kilns tend to have lower reduced sulfur emissions than longer lime kilns, though no definite correlation could be established. The probable reason is that short lime kilns must operate at higher average temperatures throughout than the long kilns to achieve an equivalent degree of calcination. The result is a more complete oxidation of reduced sulfur compounds. An additional factor is that the evolution of Na_2S at low temperatures in oxidizing atmospheres promotes H_2S formation; its evolution at higher temperatures promotes SO_2 formation (13).

Limited data indicate that reduced sulfur emissions from fluidized bed calciners are minimal. This may be due to the relatively long retention time at uniformly high temperature which provides for efficient oxidation of the sulfur compounds (14). One test shows an emission rate of less than 0.01 kg sulfur per metric ton of pulp (0.02 lb/ton). Flash drying of the mud tends to minimize H_2S formation in the fluidized bed units.

The burning of digester and evaporator noncondensable gases in the lime kilns brings an additional source of sulfur compounds to the units. The conversion of these materials to SO_2 is essentially complete because they are added with the primary air at the hot end of the lime kiln and so have sufficient retention time for complete combustion to take place (15). The addition of green liquor dregs with the lime mud to the cold end of the lime kiln can substantially increase the reduced sulfur emissions, because these materials are normally contaminated with Na_2S from the green liquor. There is also insufficient retention time at high enough temperatures for complete oxidation to take place.

11.4.4 Sulfur and Nitrogen Oxides

The concentrations of sulfur oxides in lime-kiln exhaust gases are normally minimized because the CaO can act as an efficient adsorption and reaction medium to form $CaSO_3$ and $CaSO_4$. Long kiln length, with sufficient oxygen and high calcination efficiencies, promote efficient SO_2 removal. To date, no adverse effects on lime kiln operating efficiency were traced to the sulfur released by the burning of either residual fuel oil or noncondensable gases. In a limited series of tests, it was not possible to measure the presence of SO_2 in the exhaust gases of a fluidized bed calciner, probably because the calcining and flash drying provided a two-stage removal system.

Galeano and Leopold (16) report that the lime kiln is the only major process source where significant quantities of nitrogen oxides can be measured. The primary reasons for the presence of oxides of nitrogen are that there is sufficient excess air at a temperature of 1200 to 1300° C (2200 to 2400° F) to promote the reactions. The amounts of nitrogen oxides formed in the fluidized bed calciners are probably significantly less than from rotary kilns because of the lower operating temperatures of 825 to 875° C (1500 to 1600° F). To date, no specific tests have been conducted to determine the amount of oxides of nitrogen in fluidized bed calciner exhaust gases.

11.5 Oxygen Addition

Modecular oxygen can be added to the combustion air of a lime kiln to control H_2S generation from the lime mud in the combustion zone. The oxygen must be added together with the primary air to the firing zone at the dry end of the lime kiln. This practice will promote effective mixing with the combustion gases and will provide for complete oxidation of any H_2S released from the mud. Precautions should be taken to assure that overheating of the kiln does not occur in localized areas. Such overheating could damage refractory materials, interfere with kiln operation, or result in increased emissions of oxides of nitrogen.

There is very limited field experience, to date, with the addition of oxygen to lime kilns for reducing H_2S emissions. Singman (17) reports that oxygen addition to lime kilns can substantially increase the lime mud throughput rates for previously overloaded lime kilns without excessive lime losses. An addition of 0.454 kg (1 lb) of oxygen results in a net decrease in lime makeup rate of 1.8 kg (4 lb) as CaO and, consequently, a considerable savings in operating costs for causticizing. Decreases in H_2S emissions may result for relatively short lime kilns, particularly where higher temperatures are maintained at the wet end. Additional process variables that would affect H_2S emissions in addition to kiln length include kiln diameter, mud washing efficiency and inlet sulfide level, mud firing rate and solids concentration, and gas velocities at different locations in the kiln.

11.6 Process Economics

The primary economic factor to consider for effective air pollution control of lime-calcining systems is the installation of devices for particulate control. The respective capital and operating costs for impingement and venturi scrubbing devices are presented in Table 11-5 (4).

Gaseous emission control does not normally require substantial capital investment unless flash drying of lime mud must be instituted. Maintenance of sufficient excess air, proper washing of lime mud, and the use of fresh water normally are sufficient to minimize gaseous

TABLE 11-5
CAPITAL AND OPERATING COSTS FOR LIME KILN PARTICULATE SCRUBBERS (4)

Cost Item		Scrubber Type	
		Impingement	Venturi
Capital cost,*	$/daily t pulp	30-33	22-27
	($/daily ton pulp)	(27-30)	(20-25)
	$/daily t lime	99-110	71-93
	($/daily ton lime)	(90-100)	(65-85)
Annual operating cost,**	$/t pulp	3-7	7-11
	($/ton pulp)	(3-6)	(6-10)
	$/t lime	11-22	22-38
	($/ton lime)	(10-20)	(20-35)

*Based on 1966 data.
**Based on 0.9 cents/kWh.

emissions. Addition of NaOH to the particulate scrubber makeup water to minimize H_2S emissions by increasing liquid pH levels will increase operating costs.

11.7 Lime Dust Handling

A minor source of fugitive particulate emissions from the causticizing system of a kraft pulp mill consists of lime dust releases from storage tanks and bins, and conveying and transfer facilities. Activities where lime dust is loaded or unloaded, dumped, or transferred are particular problems because of the dryness of the material that is handled. The lime dust is a localized emission source within the immediate area of the causticizing plant.

The three major approaches to control fugitive lime dust emission are to:

1. Confine the potential emission sources to prevent air leakage,
2. Wet the dust to prevent its becoming airborne by wind or by transfer operations, and
3. Use special air pollution control equipment.

The first method is effective in limiting the potential sources or fugitive emissions by effective housekeeping. It also facilitates the subsequent installation of particulate air pollution control equipment. Wetting the dust is effective in controlling fugitive dust emissions, but it can make the lime difficult to handle if overdone. It generally is not recommended as an effective technique for controlling lime dust emissions.

The third method for controlling dust emissions from lime storage and transfer facilities involves the use of particulate control techniques, such as centrifugal separation, liquid scrubbing, and fabric filtration. Keeping the dust as dry as possible facilities its recovery; therefore, liquid scrubbing is undesirable. Centrifugal collectors are not advantageous in that they require high pressure drops and tend to have low collection efficiencies.

The only known installation for particulate lime dust recovery from storage facilities employs a fabric filter baghouse for a 907 metric ton per day (1000 ton/day) kraft pulp mill. The air vents from the lime storage tanks are vented into a central duct and passed to a baghouse with a design flow rate of 4,400 m^3/h (2,600 cfm) at a maximum temperature of 290° C (550° F). The filter bags have a total surface area of 121 m^2 (1,300 ft^2) with a cleaning cycle of once each 20 minutes. The filter bags are made of a siliconized glass cloth with a design ratio of air to cloth filter area of 22.8 to 27.4 $m^3/h/m^2$ (1.25 to 1.50 cfm/ft^2).

Total capital cost for the system was $5,900 in 1966. The fans have a total capacity of 13.4 kW (18 hp) with a resultant direct annual operating cost of $1,080 per year. The system can recover 225 to 450 kg/day of lime (500 to 1,000 lb/day), which is equivalent to an annual savings of $1,800 to $3,600, based on a lime price of $22/t ($20/ton) (18, 19).

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CHAPTER 12

SMELT DISSOLVING TANK

The smelt dissolving tank is a large vessel located below the recovery furnace. A molten mixture, primarily of sodium sulfide and sodium carbonate (smelt), is continuously removed from the floor of the recovery furnace. The smelt is mixed with water in the smelt tank to produce green liquor. The smelt tank is an open, agitated vessel, covered by a hood from which large volumes of steam are emitted when the molten smelt and water mix. The smelt tank, along with the recovery boiler and lime kiln, is one of the main particulate matter sources in the Kraft pulp mill. In addition, the smelt tank can be a source of TRS emissions.

12.1 Smelt Dissolving Tank Particulate Matter Emissions

Particulate matter consisting of both dissolved and undissolved NaOH, Na_2CO_3, and Na_2S is emitted from the smelt tank with the rising flow of gases. Table 1-6 indicates that typical smelt dissolving tank particulate emissions are 0.01-0.5 kg per metric ton of pulp (0.02-1.0 lb/ton) following control devices. The majority of the smelt tanks that are controlled use simple mist eliminator pads to filter the particulate matter from the escaping vent gases (1).

The mist eliminator pads consist of fine wire mesh screens, approximately 30 cm (1 ft) thick. Droplets condense from the gas on the wire mesh and are washed back into the dissolving tank by water sprays. As may be seen from Table 12-1, typical pad efficiency for particulate matter removal is about 70-90%.

A higher collection efficiency can be achieved by following the mist eliminator with a spray or packed tower scrubber. Alternatively, some mills have low pressure drop venturi scrubbers 15-20 cm (6-8 in) of water, cyclone spray scrubbers or packed towers for particulate control without mist eliminator pads. One such packed tower gave 98% collection efficiency (Table 12-1).

It is possible to combine the vent gases from the smelt tank with the main flue gases from the recovery boiler prior to a recovery boiler particulate collection device. One expected difficulty with this approach would be the effect of the water vapor content of the smelt tank vent gases on recovery boiler particulate matter collection efficiency in an electrostatic precipitator. A second potential problem would be the likelihood of H_2S formation when the Na_2S entrained in the smelt tank vent gases come into contact with the recovery boiler CO_2.

TABLE 12-1
SMELT DISSOLVING TANK PARTICULATE MATTER CONTROL DEVICES (1)

Control Device	Collection Control Efficiency	Emission Rate	
	Percent	kg/t	(lb/ton)
Pad entrainment	71.8	0.026	(0.052)
Separator	77.2	0.075	(0.15)
	77.8	0.32	(0.63)
	90.2	1.2	(2.3)
	93.4	0.6	(1.2)
	70.8	0.79	(1.58)
Pad plus shower scrubber	96.2	0.21	(0.41)
Pad plus packed scrubber	91.9	0.60	(1.20)
Packed scrubber	98.4	0.025	(0.05)

Another combined treatment method for smelt tank vent and recovery boiler gases would be an electrostatic precipitator and scrubber combination. As discussed in Section 10.8.1, a tail end scrubber can offer significant benefits from a heat recovery standpoint. In cases where "snowing" from the precipitator occurs, a tail end scrubber can also offer significant particulate matter collection advantages. Introduction of the smelt dissolving tank vent gases after the precipitator and prior to the scrubber is possible, with additional heat recovery benefits.

Particulate matter control, as such, has not yet been required for smelt tanks in Scandinavia, although some mills use indirect condensers to recover heat from the smelt tank vent gases. The condensate is returned to the smelt tank and the warm water produced is used for washing. The feasibility of designing for heat recovery in combination with particulate control is enhanced by increasing fuel costs.

12.2 Smelt Dissolving Tank TRS Emissions

The presence of some reduced sulfur compounds (Na_2S) in the smelt proper, and occasionally some reduced sulfur gases from the recovery furnace, can cause TRS emissions from the smelt tank vent. The amount of such gases is highly variable, reported to range from the equivalent of 0 to 1.85 kg H_2S per metric ton of pulp (0-3.7 lb/ton) (1). Variables that effect the TRS emission rate are the sulfide content of the particulate matter in the vent gases, the turbulence in the dissolving tank, the type of solution used in a scrubber, if present, and the pH of the scrubber liquor (2). The effect of some of these variables is illustrated in Table 12-2. This table, prepared from a NCASI special study in 1970-1971 (2), indicates that the most effective TRS control was wet scrubbing with fresh water.

TABLE 12.2
TRS EMISSIONS FROM SMELT DISSOLVING TANKS (2)

Mill	TRS		Control Device	Scrubbing Solution
	kg/t	(lb/ton)		
II	0.005	0.01	None	–
III	0.06	0.12	Packed Tower	Weak Wash and Contaminated
	0.005	0.01	Packed Tower	Fresh Water
	0.005	0.01	Spray	Fresh Water
IV	0.02	0.04	Showers	Fresh Water
	0.02	0.04	Showers	Fresh Water
	0.04	0.08	Demister	Fresh Water
	0.055	0.11	None	Fresh Water
V	0.005	0.01	Demister	Fresh Water
	0.01	0.02	None	–
	0.0005	0.001	Demister	Fresh Water
	0.0005	0.001	None	–
VI	0.005	0.01	Demister	Fresh Water
	0.005	0.01	None	–
	0.0005	0.001	Demister	Fresh Water
VII	0.01	0.02	Showers	Fresh Water
	0.015	0.3	Showers	Fresh Water
VIII	0.005	0.01	Demister	Contaminated Condensate
IX	0.0005	0.001	None	–
X	0.01	0.02	Demister	Fresh Water
	0.005	0.01	Demister	Fresh Water
	0.0005	0.01	Demister	Fresh Water
XI	0.0005	0.001	Packed Tower	Weak Wash
XII	0.005	0.01	Demister	Weak Wash and Contaminated Condensate
	0.005	0.01	Demister	Weak Wash and Contaminated Condensate
XVII	0.005	0.01	Showers	Fresh Water

Weak wash from the lime mud clarifier, lime mud washing filtrate and evaporator condensates are used as well as fresh water for scrubber liquor. Increased organic sulfides were found when evaporater condensates were used. A small amount of hydrogen sulfide was liberated from lime mud clarifier supernatant in some systems, probably because of acidification of the scrubbing liquor (3).

Recently, addition of caustic to smelt tank scrubbers has been suggested for improved TRS control (4). In one mill, caustic will be added to clean evaporator condensates to be used as smelt tank scrubber liquor. The scrubbing liquor will then be used for lime mud washing (5).

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CHAPTER 13

EMISSIONS OF OXIDES OF NITROGEN, HYDROCARBONS, AND WATER VAPOR

Additional pollutants from the kraft pulp mill include oxides of nitrogen and hydrocarbons. Oxides of nitrogen can be emitted from combustion sources, such as the recovery furnace, the lime kiln of the chemical recovery system, and the power boilers. Hydrocarbons and other organic nonsulfur compounds can be emitted in varying quantities from the digester, washers, evaporators, and direct contact evaporators. Both types of pollutants may have potential significance to photochemical air pollution when acting together. Water vapor is also emitted in varying quantities from all kraft pulp mill sources. Condensation of water vapor into a visible plume may present some hazard if the plume restricts visibility adversely, such as across a highway, airfield, or harbor.

13.1 Nitrogen Oxides

Nitrogen oxides are formed by the reaction of atmospheric nitrogen and oxygen at elevated temperature when fuels are burned. Nitrogen oxides also can form from the oxidation of nitrogen which is present as a trace constituent in fuels. The major oxides of nitrogen formed during combustion processes are nitric oxide (NO) and nitrogen dioxide (NO_2). Their chemistry of formation is as follows:

$$N_2 + O_2 \rightarrow 2NO$$

$$2NO + O_2 \rightarrow 2NO_2$$

The nitrogen oxides present in exhaust gases from combustion processes normally are 90 to 95 percent by volume NO, and 5 to 10 percent by volume NO_2.

The primary variables affecting the rate and degree of formation of nitrogen oxides during combustion processes are the flame temperature and the oxygen content of the gas in the flame zone. The degree of nitrogen oxide formation tends to increase exponentially with temperature above about 1300° C (2400° F), particularly when the oxygen concentration in the combustion zone is two percent by volume or greater (1). The rate of NO formation increases sharply with temperature, as shown in Table 13-1 (2).

The major variables that can influence the nitrogen oxide formation during thermal oxidation processes include the flame temperature, oxygen content in the flame zone, fuel nitrogen content, and combustion unit configuration. Flame temperature is increased by

TABLE 13-1
EFFECT OF FLAME TEMPERATURE ON NITRIC OXIDE EQUILIBRIUM CONCENTRATION AND REACTION TIME (2)

Gas* Temperature °C	Gas* Temperature (°F)	NO Concentration ppm, by volume	Reaction Time sec
2430	(4400)	19,000	0.004
1930	(3500)	14,000	0.090
1760	(3200)	4,000	0.7
1430	(2600)	500	21.0
1090	(2000)	10	162.0

*Reactant gases: 77% N_2, 15% O_2, and 8% inerts.

increased fuel heating value, but decreases with increasing fuel moisture content. The heat release rate and combustion volume available for heat release also influence flame temperature. Both black liquor and lime mud tend to have moisture contents of 30 to 40 percent by weight, which act to inhibit increases in flame temperature because the water acts as a heat sink. The fuel nitrogen content of both of these fuels is relatively low, 0.1 to 0.5 percent by weight for black liquor and negligible for lime mud.

The fuel nitrogen content is the primary variable limiting NO emissions at temperature below 1100° C (2000° F); while flame temperature becomes dominant above 1300° C (2400° F) (3).

Galeano and Leopold (4) report that nitrogen oxide concentrations from kraft pulp mill sources are relatively low when compared to power boilers and are higher from lime kilns than from recovery furnaces, as listed in Table 13-2.

Nitrogen oxide emissions in both cases can be minimized by operating combustion units at minimum excess air, minimum flame temperatures, and maximum fuel moisture contents.

13.1.1 Kraft Recovery Furnaces

The configuration of the combustion unit is an important factor in determining potential nitrogen oxide emissions from kraft pulp mill combustion sources. Kraft recovery furnaces have relatively large volume rectangular combustion chambers and relatively low heat release rates of 170 to 340 MJ/h per m^3 (4,500 to 9,000 BTU/hr per ft^3), which act to inhibit high flame temperatures. The fuel has a relatively low heating value of 14 to 16 MJ per kg dry solids (6000-7000 BTU/lb). Black liquor has a high moisture content of 30 to 40 percent by

TABLE 13-2
NITROGEN OXIDE EMISSIONS FROM KRAFT PULP MILL PROCESS SOURCES (4)

			NO_x Concentration		Emission Rate	
Process Unit	Temperature		Average	Range	Average	Range
	°C	(°F)	ppm, by vol.		kg NO_x/t (lb/ton)	
Recovery furnace	1010-1230	(1850-2250)	32	0-53	3(6)	0-5 (0-10)
Lime kiln	1260-1390	(2300-2530)	200	113-260	18(36)	10-25 (20-50)

weight that inhibits flame temperature rise. Flame temperatures are about 980 to 1260° C (1800 to 2300° F) for normal operation in a kraft recovery furnace.

In addition, the endothermic reduction of Na_2SO_4 to Na_2S in the smelt bed of the recovery furnace also acts as a heat sink to inhibit excessive flame temperatures. Another built-in control method is that the air flow is split between primary and secondary zones, and sometimes a tertiary zone. A reducing atmosphere above the smelt bed also acts to remove oxygen from the combustion zone to inhibit the formation of nitrogen oxides. Introducing tangential air into the furnace can act to spread out the flame front and, in that way, also inhibit the increase in gas temperature. As a result of inhibiting both flame temperature and oxygen level in the combustion zone, the nitrogen oxide levels normally range from 0 to 50 ppm by volume.

13.1.2 Lime Kilns

Lime kilns are used to burn a mud containing $CaCO_3$ to recover CaO by addition of natural gas or fuel oil. The fuel and air are added countercurrently with the mud at opposite ends of a long cylindrical rotary kiln, resulting in a maximum temperature of 1260 to 1430° C (2300 to 2600° F) at the fuel addition end of the kiln and a temperature of 200 to 315° C (390 to 600° F) at the lime mud addition end of the kiln. The lime mud contains 30 to 40 percent water by weight. Most of this water has been evaporated by the time the mud reaches the hot end of the kiln and does not exert as great a suppressing effect on flame temperature as does the black liquor in a recovery furnace. The firing zone is narrower and is concentrated with less lateral turbulence in the lime kiln, producing higher flame temperatures. As a result, higher nitrogen oxide concentrations exist in flue gases from lime kilns than from recovery furnaces in kraft pulp mills.

13.1.3 Power Boilers

Steam is required in pulp mills for process and space heating, driving equipment, and generating electricity. Although significant quantities of steam are generated in recovery furnaces, conventional industrial boilers supply much of the steam required by a pulp mill. Power boilers are the largest sources of nitrogen oxides in pulp mills. Table 13-3 lists some values of nitrogen oxide concentrations from kraft and NSSC pulp mill power boilers. Nitrogen oxide emission factors for auxiliary power boilers were presented in Table 1-8.

TABLE 13-3
NITROGEN OXIDE EMISSIONS FROM POWER BOILERS (4)

Unit	NO_x Average	NO_x Range	Temperature °C	Temperature (°F)	Excess Air
	ppm, by vol.	ppm, by vol.	°C	(°F)	%
Pulverized coal, front end, 86,000 kg/h (190,000 lb/hr)	375	310-445	1425-1480	(2600-2700)	–
Pulverized coal & bark, 32,000 kg/h (70,000 lb/hr)	205	150-280	1200-1425	(2200-2600)	–
Gas fired, 45,000 kg/h (100,000 lb/hr)	436	325-535	–	–	33
Gas fired, 100,000 kg/h (220,000 lb/hr)	190	161-232	870-980	(1600-1800)	46
Bark fired, 122,000 kg/h (270,000 lb/hr)	123	101-145	1040-1140	(1900-2080)	89

13.2 Water Vapor

Water vapor is emitted in varying quantities from all kraft pulp mill sources. Water vapor can be considered as an air pollutant under certain circumstances, such as when it acts to reduce visibility in highly humid or cold atmospheres or acts to modify climate or rainfall. Water vapor emissions also represent a potential loss of heat energy that might otherwise be recovered by condensation to reduce overall plant energy consumption.

Crabtree (5) reports that the potential loss of water vapor to the atmosphere from kraft pulp mill operations is about 5 to 8 t of water per metric ton of air dried pulp produced (5 to 8 ton/ton). The major potential sources of water vapor released to the atmosphere are the recovery furnace and the paper machines, as shown in Table 13-4 (5).

The loss of water vapor from kraft pulp mill sources is affected by process operating factors, water reuse and recycling practices, and the relative efficiencies of heat recovery systems. The use of efficient heat recovery systems for digester blow gases and multiple-effect evaporators tends to reduce the amount of water vapor released to the atmosphere. The use

TABLE 13-4
WATER VAPOR EMISSIONS TO THE ATMOSPHERE FROM KRAFT PULP MILL SOURCES (5)

Source	Moisture Content %, by vol.	Water Emission Rate kg H_2O/t	 (lb H_2O/ton)
Batch digester	30-99	100-250	(200-500)
Multiple evaporator	50-99	500-1000	(1000-2000)
Recovery furnace	25-35	2200-2500	(4400-5000)
Smelt tank	35-45	150-250	(300-500)
Lime kiln	25-35	350-750	(700-1500)
Paper machines	5-15	1700-2500	(3400-5000)
Total		5000-7250	(10000-14500)

of indirect contact surface condensers also minimizes the amount of water used in the cooling processes. The use of cooling towers for heat dissipation tends to provide an additional source of water vapor emissions to the atmosphere if water is recycled. Fuel savings in reduced steam usage can range from $0.55 to $3.30 per metric ton of pulp ($0.50 to $3.00/ton) by effective use of heat transfer equipment and water reuse practices (6).

Evaporation of process fuels to high solids concentrations prior to burning results in less water vapor emission to the atmosphere. Evaporation of black liquor to 65 to 70 percent solids by forced circulation evaporation can improve the heat economy of the kraft recovery system. Concentration of lime mud to 68 to 70 percent solids prior to firing in the lime kiln reduces the water vapor release rate from the firing zone. The kiln exhaust gas from a scrubber must be cooled to below 65° C (150° F) to achieve an actual reduction in water vapor emission from the lime kiln that is sufficient to compensate for possible water evaporation in the liquid scrubber.

The two major techniques employed, to date, for controlling local water vapor levels in ambient air are condensation to prevent its release to the atmosphere and dispersion resulting from high stack gas velocity or tall stacks. Dispersion of moisture plumes by means of elevated discharges may be particularly necessary for kraft pulp mills located near highways, airports, harbors or populated areas to alleviate potential fog. The presence of large quantities of particulate matter in ambient air can act as condensation nuclei to accelerate the formation of fog and inhibit its dispersal where an additional source of water vapor already exists.

Shumas and Hansen (7) describe a system where flue gases from the recovery furnaces and bark-fired power boilers at a 1,135 metric ton per day (1250 ton/day) kraft pulp mill are piped 0.8 km (0.5 mile) to a stack 62 m high (200 ft) and discharged 258 m (850 ft) above the valley floor. The purpose of the stack is to discharge the moisture plume above the level of the normal winter inversions in the narrow valley so as to alleviate any potential fog formation problems, such as interference with aircraft landings and takeoffs. Plume rise above the top of the stack ranges from 90 to 210 m (300 to 700 ft), depending on stack gas flow rate and temperature and the season of the year.

Flue gases from the respective combustion units are passed through a venturi scrubber with a flow rate of 510 m^3/h (2250 gpm) and are cooled to 50° C (125° F). The gas then flows through a wood stove cylindrical duct 4.9 m (16 ft) in diameter at a flow rate of 620 m^3/s (1.3 million cfm) with a fan discharge gauge pressure ranging from 6.3 to 31.8 cm of water (2.5 to 12.5 in water).

The capital cost, including all engineering fees, for the system is about $6,500,000 to $7,000,000. The system is powered by two parallel turbine drive booster fans of 2050 kW (2,750 hp) each. At an electric power cost of $67/kW/year ($50/hp/year), the operating costs are computed as $275,000 per year for the fans.

A system recently was placed in operation at a kraft pulp mill to alleviate moisture plume problems from three parallel paper machine drier vents near a major interstate highway (8). The exhaust gases total 230,000 m^3/hr (135,000 cfm) with a temperature of 46° C (115° F) and a moisture content of 10 to 15 percent by volume. The gases are collected and passed through a central fan of about 112 to 150 kW (150 to 200 hp), then through a cylindrical metal stack 25 m high (80 ft) with an exit diameter of approximately 2 m (6 ft), resulting in an exit gas velocity of 22-30 m/s (75-100 fps). The capital cost for the system is about $80,000; the annual direct operating cost approximately $10,000, based on $67/kW/year ($50/hp/year).

13.3 Organic Compounds

Organic compounds other than those containing sulfur are also emitted in varying quantities from several types of processing units in kraft pulp mills. For a discussion of nonsulfurous organic compounds, see section 1.1.3.

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CHAPTER 14

AIR POLLUTION CONTROL IN SULFITE PULP MILLS

Even though many technological similarities exist between the sulfite and the sulfate or kraft process, the air pollutants generated in each of these processes are quite different. The sulfite process usually operates with acidic SO_2 solutions and, therefore, SO_2 is the main gaseous air pollutant. In certain special cases of alkaline sulfite liquor burning in recovery boilers where chemical reduction may take place, H_2S may also be emitted. Organic reduced sulfur compounds are not produced. Since the odor threshold is roughly one thousand times higher for SO_2 than for reduced sulfur compounds, odors generated in the sulfite pulp mill will generally be much less than in the kraft process. The sulfite process will also emit particulate matter from spent liquor burning.

Even within the sulfite industry itself, there are many differences in SO_2 and particulate emissions because of differences in cooking liquor bases, acidities, and recovery methods.

14.1 Sulfite Pulping Processes

14.1.1 General

Sulfite pulping is practiced with numerous modifications. Cooking can be done with different bases, namely calcium (Ca), magnesium (Mg), ammonium (NH_4), and sodium (Na).

Cooking can be done:

1. At different pH levels, from acidic to alkaline, subject to the solubility constraints imposed by the base used;
2. In several stages with changes in cooking liquor between;
3. With a high yield of pulp and with additional mechanical defibration (the neutral sulfite semi-chemical processes).

The main sulfite pulping processes, pH range, principal cooking liquor composition, and bases are presented in Table 14-1. This table also lists the allowable pH range for the different bases.

The potential for release of SO_2 into the atmosphere increases with decreasing pH.

TABLE 14-1
MAIN SULFITE PULPING PROCESSES

Cooking Method	pH Range	Cooking Liquor	Base Alternatives
Acid bisulfite	1-2	$M(HSO_3)_2$, SO_2	M = Ca, Mg, $(NH_4)_2$, Na_2
Bisulfite	2-6	$M(HSO_3)_2$	M = Mg, $(NH_4)_2$, Na_2
Neutral sulfite	6-9	MSO_3, MCO_3	M = $(NH_4)_2$, Na_2
Alkaline sulfite	10-12	MSO_3, $M(OH)_2$, MS	M = Na_2
Two-stage	6-8 and 1-4	MSO_3, $M(HSO_3)_2$, SO_2	M = Na_2
Two-stage	2 and 5-8	$M(HSO_3)_2$, SO_2, MSO_3	M = Na_2
Three-stage	4 and 2 and 8	$M(HSO_3)_2$, SO_2, MSO_3	M = Na_2

The cost of chemicals and the possibility of chemical recovery provide more information on the emission potentials of the different sulfite processes. Based on different chemical prices, combustion products and recoveries of chemicals, calcium-based processes have the highest air pollution potential, ammonium-based processes next, and magnesium- and sodium-based processes are the least polluting, see Table 14-2.

TABLE 14-2
SULFITE PROCESS CHEMICALS, PRICE, COMBUSTION AND RECOVERY

Base	Relative Price Per Mole	pH Range	SSL* Combustion Dust or Smelt	Gas Products	Chemicals Feasibly Recovered
Ca	1/7	1-2	$CaSO_4$, CaO, $CaCO_3$	SO_2	None
Mg	2/3	1-6	MgO	SO_2	MgO + SO_2
NH_4	3/4	1-9	None	SO_2, N_2, NO_X	SO_2
Na	1	1-12	Na_2S, Na_2CO_3	SO_2, H_2S	Na_2S, $NaCO_3$

**Spent Sulfite Liquor.*

Many sulfite mills continue to dispose of their spent sulfite liquor (SSL) to receiving waters. These are primarily calcium-based mills, but some magnesium-based mills and a number of NSSC mills using ammonium or sodium practice this disposal technique. These mills are usually old and though they will have less SO_2 emission than similar mills with SSL recovery, their water pollution contribution through SSL dumping is so great that major mill modifications, or in some cases, closures, may be required to comply with water pollution regulations.

14.1.2 Atmospheric Emissions from Different Sulfite Processes

Typical SO_2 and dust emissions for different Scandinavian sulfite processes are given in Table 14-3. Examples of the typical SO_2 and particulate emissions from United States sulfite pulp mills are presented in Table 14-4.

TABLE 14-3
SCANDINAVIAN SULFITE PULP MILL EMISSIONS (1)

	Mill Number								
Parameter	1	2	3	4	5	6	7	8	9
Base	Ca	Ca	Mg	Mg	Na	Na	Na	NH_4	NH_4
Cooking pH	1-2	1-2	1-2	3-5	3-5	3-5	3-5	3-5	3-5
Cooking yield, %	50	50	55	55	50	75	75	75	75
SSL collection, %	0	70	85	85	90	0	85	0	80
SSL evaporation	No	Yes	Yes	Yes	Yes	No	Yes	No	Yes
SSL combustion	No	Yes	Yes	Yes	Yes	No	Yes	No	Yes
Chemicals recovery	No	No	Yes	Yes	Yes	No	Yes	No	No
Sulfur losses, $kgSO_2/t$									
Washing loss	210	56	20	40	15	100	16	100	16
Spills	0	20	10	10	10	0	10	0	10
Condensates	0	26	15	110	10	0	8	0	8
Gaseous loss	10	10	10	2	2	2	2	2	2
Flue gases	0	83	15	25	20	0	14	0	74
Flue gas dust	0	25	0	0	0	0	0	0	0
Sulfur make-up, kg SO_2/t	220	220	70	87	57	100	50	100	100
Total SO_2 emission, kg SO_2/t	10	93	25	27	22	2	16	2	76
Flue gas dust, kg dust/t	0	90	70	100	20	0	10	0	0
Dust collection, %	0	80	99	99	97	0	97	0	0
Dust emission, kg dust/t	0	18	1	1	1	0	0	0	0

TABLE 14-4
TYPICAL POTENTIAL AMERICAN SULFITE PULP MILL EMISSIONS (2)

Parameter	Mill Number 1	2	3	4
Base	Ca	Mg	Mg	NH_4
Type	acid sulfite	acid sulfite	bisulfite	acid sulfite
Cooking yield, %	45	43	50	50
SSL evaporation	No	Yes	Yes	Yes
SSL combustion	No	Yes	Yes	Yes
Chemicals recovery	No	Yes	Yes	No
SO_2 emissions, kg SO_2/t				
Digester blow	75	8.5	8.5	1.5*
Washers and screens	–	2	2	2
Evaporators	–	2.5	2.5	5
Boiler	–	9.5	10**	200
Acid towers	2.5	–	–	0.25
Particulate matter emissions, kg/t	0	1	1	1.5

*Packed tower absorber with 91% SO_2 removal.
**Venturi absorber after recovery boiler.

In the following sections, the air pollutants generated in the basic sulfite process operations, from digestion to cooking acid preparation, are discussed, and the effects of different bases and acidities are treated separately for each basic operation.

The general treatment for SO_2 emissions is scrubbing with alkaline solutions. The recovery of SO_2 is a function of pH and gas film resistance, and usually exceeds 90 percent.

Different dust separation methods can be used for collecting particulate matter. The three most widely used are cyclones, scrubbers and electrostatic precipitators.

14.2 Digester Gases

Sulfite cooking is performed both in batch digesters and in continuous digesters, the former being more prevalent. The continuous digester causes no air pollution problem; the batch digester may release substantial amounts of SO_2 depending on the blow system and cooking acid pH.

14.2.1 Batch Digesters

Acid bisulfite cooking in batch digesters creates high SO_2 pressures in the digester; bisulfite and neutral sulfite cooking have correspondingly lower pressures. Digester relief and blow cause SO_2 emissions.

SO_2 and cooking liquor are relieved from the digester to the acid preparation accumulator system in several steps, top relief, side relief, high-pressure blowdown, and, finally, low-pressure blowdown. All the SO_2 relief is recovered in the acid preparation system (section 14.7). For bisulfite and neutral sulfite cooking, the SO_2 pressure in the digester is lower and a less elaborate relief system will return the SO_2 to acid preparation. The digester relief will, therefore, usually not constitute an air pollution problem for any base or for any pH range.

The digester can be emptied in two ways. The usual North American practice is to relieve the digester down to a certain blow pressure, (.14-.28) MPa (20-40 psig), and them blow the contents into the blow pit. This procedure is called hot blow (Figure 14-1).

The European practice is to relieve the digester down to atmospheric pressure and then flush the contents into the blow pit by pumping spent liquor into the digester. This procedure is called cold blow.

Hot blow will release considerable amounts of SO_2 when the spent liquor is flashed, especially for acid bisulfite cooking. The SO_2 emission from the blow pit can amount to about 30 kg SO_2 per metric ton of pulp (60 lb SO_2/ton) (2, 3). The blow gas is roughly 95 percent water vapor, 3 percent SO_2, and 2 percent CO_2 (2).

One feasible treatment for the SO_2 emission is to scrub the blow gas with an alkaline solution of the base and return the solution to acid preparation. SO_2 recovery efficiencies are reported to be as high as 97 percent for this type of treatment (3). This method works well with Na and NH_4 bases. Magnesium and calcium require cumbersome slurry scrubber systems.

Another method is to scrub the blow gases with cold water to recover heat and SO_2; the SO_2 is then steam stripped from the water solution. This method is reported as being insufficient for SO_2 recovery (3).

Hot blow also may be performed in ordinary blow tanks with appropriate heat recovery systems. This is usually practiced with bisulfite or neutral sulfite cooking, either of which has much less potential for SO_2 release.

Blow pit emissions for bisulfite or neutral sulfite cooking are about 10 kg per metric ton of pulp (20 lb SO_2/ton) (2). Cold blow will show considerably smaller SO_2 release than hot

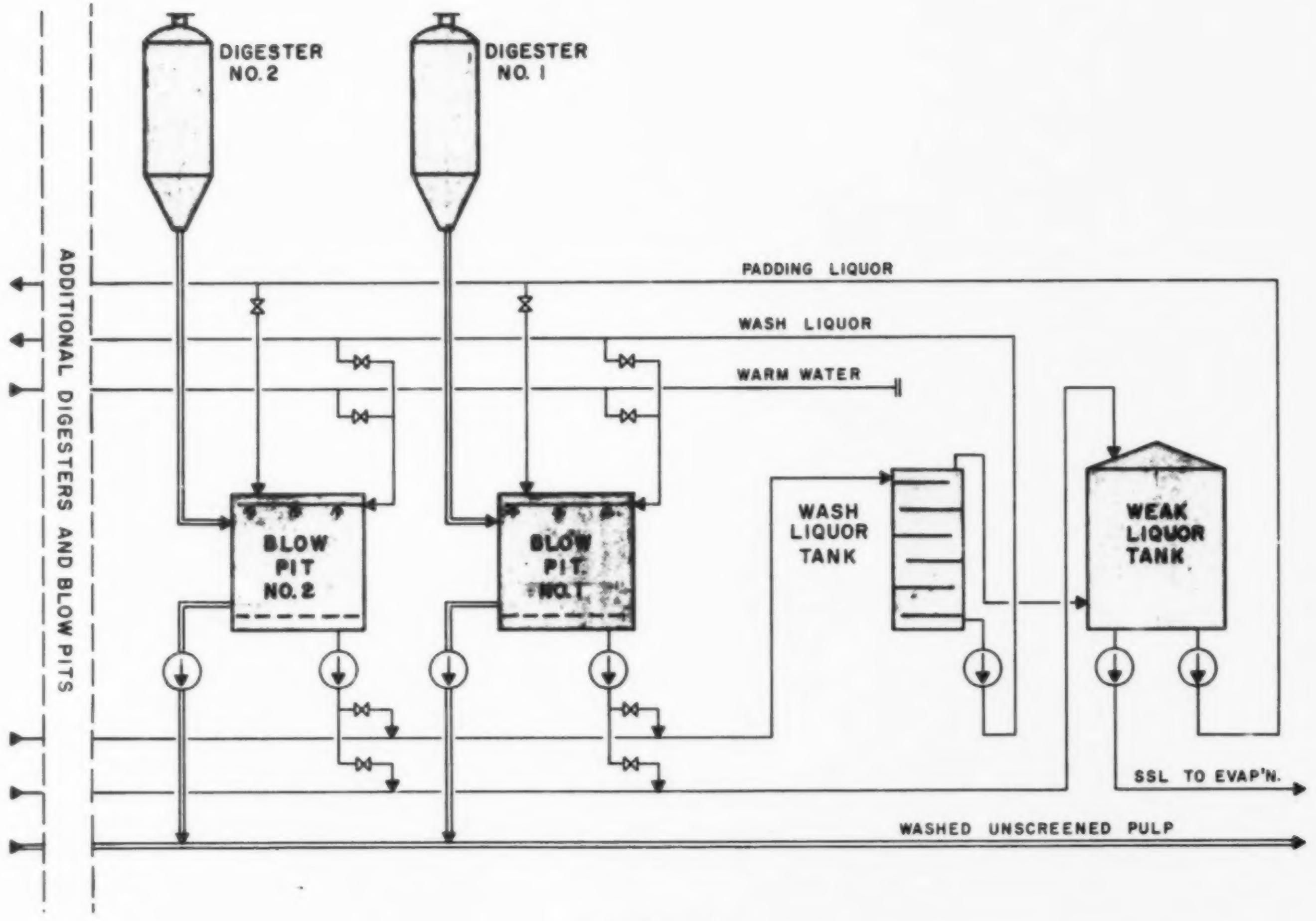
DIGESTER NO. 2
DIGESTER NO. 1
ADDITIONAL DIGESTERS AND BLOW PITS
PADDING LIQUOR
WASH LIQUOR
WARM WATER
BLOW PIT NO. 2
BLOW PIT NO. 1
WASH LIQUOR TANK
WEAK LIQUOR TANK
SSL TO EVAP'N.
WASHED UNSCREENED PULP

FIGURE 14-1

PRINCIPAL FLOW DIAGRAM FOR SPENT LIQUOR COLLECTION IN BLOW PITS, 2 STAGE DISPLACEMENT WASH blow. With acid bisulfite cooking, the SO_2 emission from the blow pit with cold blow will be 2-10 kg SO_2 per metric ton of pulp (4-20 lb SO_2/ton).

Again, the most practicable treatment is scrubbing with alkaline solution of the base. Calcium and magnesium base are not generally suitable for this application.

With bisulfite or neutral sulfite cooking, the cold blow pit SO_2 emission is less than 2 kg SO_2 per metric ton of pulp (4 lb/ton), making scrubbing impractical.

14.2.2 Continuous Digesters

The continuous digester is essentially a completely closed system cooking with magnesium, ammonium, or sodium base in the pH range 4-6. As with a kraft continuous digester, a continuous diffusion washing stage is integrated with the digester. These features make the continuous sulfite digestion process a very clean one, with negligible emissions of SO_2. The SO_2 containing gases from the presteaming vessel relief and from the flash evaporators are returned to the cooking acid preparation system.

14.3 Washer Gases

There are many different sulfite pulp washing systems. For example, pulp may be washed by displacement in the digester or in the blow pit. Additional washing in rotary drum filters or in continuous diffusers is usually necessary (Figure 14-2) because of current water pollution regulations for SSL collection efficiency and the high cost of the sodium- and magnesium-based chemicals. Typically, the SO_2 emissions from washers and screens are 8 kg SO_2 per metric ton of pulp (16 lb SO_2/ton) for bisulfite cooking and even less for bisulfite and neutral sulfite cooking. Because of the large gas flows involved in vacuum rotary drum washing, SO_2 recovery through scrubbing is not practicable. For washing methods with smaller vent gas flows, scrubbing may be used.

14.4 Evaporator Gases

The evaporation of SSL results in the release of SO_2 from the liquor. The more acidic the cooking liquor, the more SO_2 is liberated during SSL evaporation. The evaporation systems in use are the same as those used for kraft black liquor, and the multiple-effect vacuum evaporation plant is the most commonly used for both. Each evaporation effect is vented to the vacuum system, and the vacuum system vent becomes the main emission point for evaporator gases. The hotwell is the main emission point for evaporator condensates. These condensates contain SO_2 and can contribute to the evaporation plant SO_2 emission (Figure 14-3).

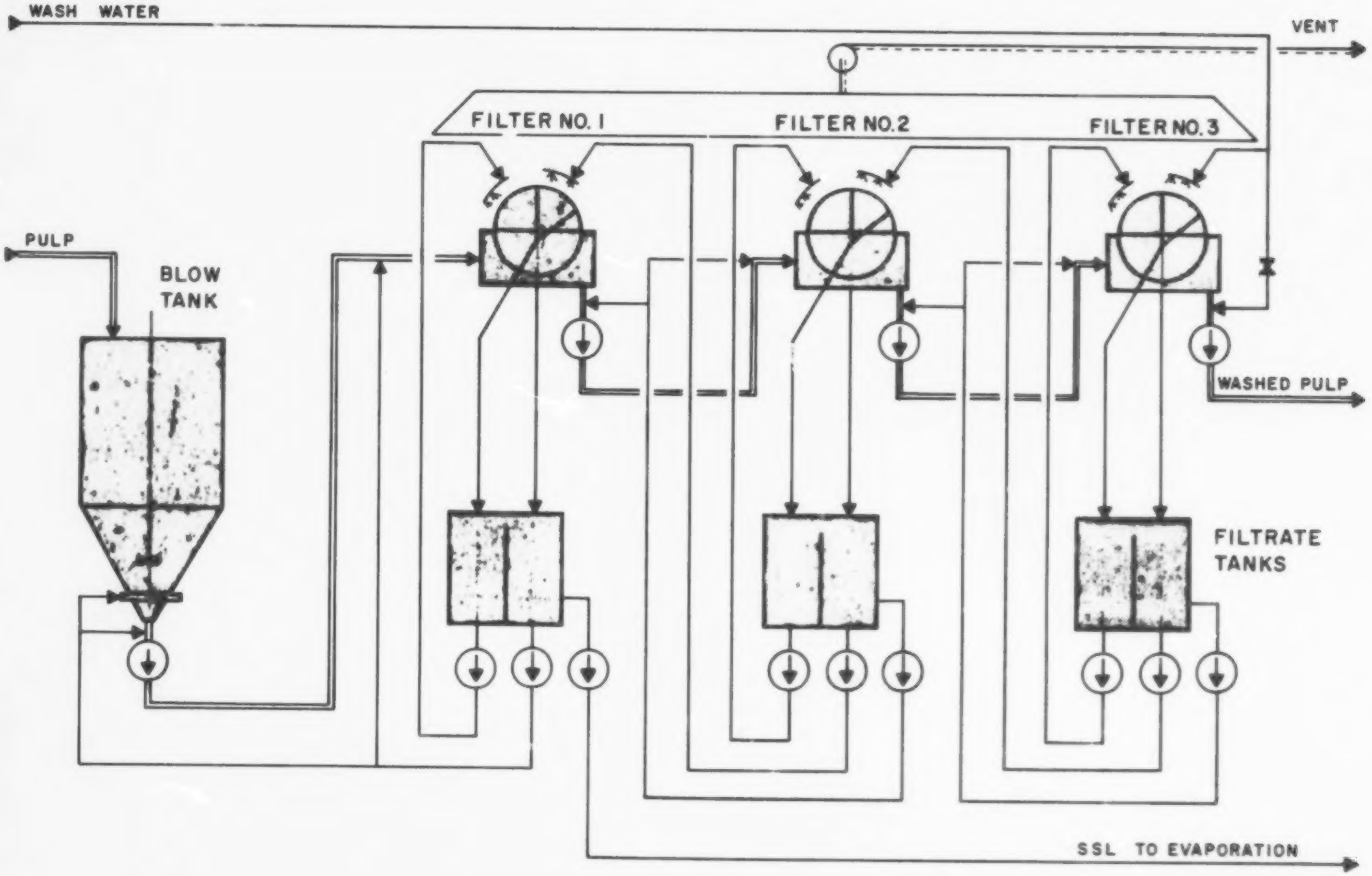
WASH WATER
VENT
PULP
BLOW TANK
FILTER NO. 1
FILTER NO. 2
FILTER NO. 3
WASHED PULP
FILTRATE TANKS
SSL TO EVAPORATION

FIGURE 14-2

PRINCIPAL FLOW DIAGRAM FOR SPENT LIQUOR COLLECTION IN ROTARY WASHER PLANT
(3 2-ZONE FILTERS)

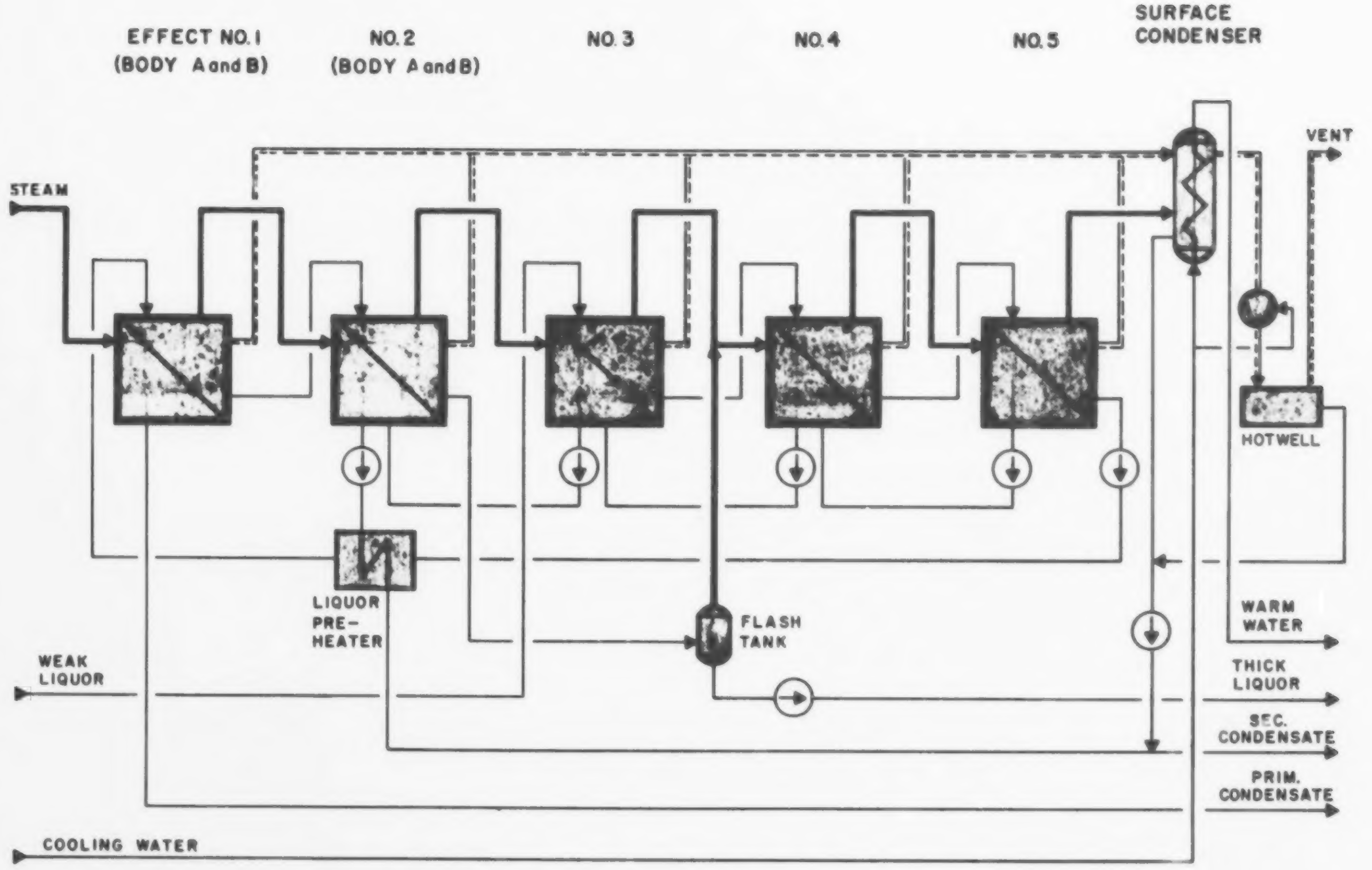
EFFECT NO. I
(BODY A and B)
NO. 2
(BODY A and B)
NO. 3
NO. 4
NO. 5
SURFACE
CONDENSER
STEAM
VENT
HOTWELL
LIQUOR
PRE-
HEATER
FLASH
TANK
WEAK
LIQUOR
WARM
WATER
THICK
LIQUOR
SEC.
CONDENSATE
PRIM.
CONDENSATE
COOLING WATER

FIGURE 14-3

PRINCIPAL FLOW DIAGRAM FOR SPENT LIQUOR EVAPORATION IN MULTIPLE EFFECT VACUUM PLANT, 5 EFFECT, 7 BODIES (SPARE BODIES NOT SHOWN)

For bisulfite and neutral sulfite cooking, the evaporator gases contain small amounts of SO_2, usually less than 1 kg SO_2 per metric ton of pulp (2 lb SO_2/ton). With acid bisulfite cooking, the evaporator gases contain 20-30 kg SO_2 per metric ton of pulp (40-60 lb SO_2/ton) (1). This significant SO_2 emission can be treated and recovered by several methods. The feasibility of each method depends on what other results can be achieved simultaneously by that particular method.

A widely practiced method of eliminating evaporator SO_2 emissions is to return the evaporator gases to the acid preparation plant to recover the SO_2.

Another method is to scrub the gases with an alkaline solution of the base and then return the solution to acid preparation. This procedure, however, requires a greater investment and is difficult with calcium and, to a lesser degree, with a magnesium base.

If the sulfite mill has a weak liquor fermentation plant, either for CH_3CH_2OH or yeast, the SSL must be neutralized prior to its use in fermentation. This can be done by stripping it in a separate evaporation stage or by adding base. After fermentation, the SSL can be evaporated with insignificant SO_2 emissions.

The weak SSL can be steam stripped in the evaporation plant, as mentioned before. The SO_2 stripped off is returned to acid preparation, and subsequent evaporation of the stripped SSL will yield very little SO_2.

The weak SSL can be neutralized by adding base, CaO, MgO, ammonia (NH_3), or NaOH, to the liquor before evaporation. This practically eliminates gaseous SO_2 emissions from the evaporation plant. SSL neutralization, however, is mainly proposed to reduce the evaporation condensate BOD by hydrolyzing acetic acid (CH_3COOH) so that the resulting nonvolatile acetate will proceed with the liquor to combustion. Full-scale neutralization trials began in Sweden in 1972, but, thus far, continuous operation over long periods of time has been difficult to maintain. Acid bisulfite cooking with magnesium base requires the addition of about 35 kg MgO per metric ton of pulp (70 lb MgO/ton) to the SSL before evaporation to raise the pH to 6.5 (4).

14.5 Combustion Gases

All sulfite process spent liquors can be burned. Calcium, magnesium and ammonium-base SSL can be burned about any supporting combustion fuel if evaporated to 55 percent dry solids, atomized thoroughly, and burned with preheated air in a separate combustion chamber ahead of the main furnace. During combustion of any SSL, emissions of SO_2 and particulates of base oxides, carbonates, and sulfates can occur, depending on the particular prevailing equilibrium conditions.

Sodium-based SSL is subject to either oxidizing or reducing combustion. In the latter case combustion is in a black liquor recovery boiler and H_2S emissions are possible. The majority of particulate matter emissions will be Na_2SO_4. Most of the sodium and sulfur is recovered in the smelt.

14.5.1 Calcium SSL Combustion Products

Collecting calcium SSL with 70 percent efficiency and burning it produces about 80 kg SO_2 and 90 kg dust per metric ton of pulp (160 lb and 180 lb/ton) (Table 14-3). The dust is about 60 percent $CaSO_4$ and 40 percent CaO, which includes some $CaCO_3$ and traces of other salts.

The flue gases are usually passed through a cyclone dust separation system with approximately 80 percent collection efficiency. The dust is stored in a pile or dumped into receiving water, because no economic use has been found for it so far (5). Better removal can be achieved by electrostatic precipitators, but they are too expensive for recovering a virtually worthless dust.

An SSL collection efficiency of 70 percent is very low, and water pollution abatement requirements may demand a smaller washing loss. Dumping calcium sulfite ash into the water also may not be permitted.

SO_2 can be removed from the flue gases by scrubbing them with CaO or $CaCO_3$ slurry. But even if all the CaO of the dust from a 100 percent flue gas dust separation could be used for this, the SO_2 emission would still be around 40 kg/t (80 lb SO_2/ton). A byproduct of this control method is about 250 kg per metric ton of pulp of a 50 percent sludge (500 lb of sludge/ton), for which no use is known.

More effective SO_2 removal requires additional lime and produces more sludge. At this point, changing the base might be a more feasible alternative.

14.5.2 Magnesium SSL Combustion Products

Collecting magnesium SSL with 85 percent efficiency and burning it produces around 15 kg SO_2/t plus 70 kg magnesium oxide (MgO)/t for acid bisulfite cooking and 25 kg SO_2/t plus 100 kg MgO/t for bisulfite cooking (30 plus 140 lb/ton and 50 plus 200 lb/ton respectively). These figures assume MgO recirculation (Table 14-3).

These emissions, however, are effectively treated in a chemicals recovery system that separates the MgO dust by cyclones and scrubbers, hydrolyzes the MgO into magnesium hydroxide slurry, and scrubs the SO_2 from the flue gases with this slurry. The net result is a small dust emission and moderate SO_2 emission, which can be further decreased by additional scrubbing stages as discussed in section 14.9.1.

14.5.3 Ammonium SSL Combustion Products

Collecting ammonium SSL with 85 percent efficiency and burning it produces around 130 kg SO_2/t (260 lb SO_2/ton) for bisulfite cooking. During combustion, the NH_3 is converted to water and nitrogen (N_2), and consequently the base is lost. Scrubbing SO_2 from the flue gas with fresh ammonia solution has been successfully demonstrated in at least two American ammonium-based mills (6, 7). The nature of any air pollution problems related to the nitrogen compounds emitted from ammonium-based pulping is discussed in section 14.10.

14.5.4 Sodium SSL Combustion Products

Sodium SSL burning may yield various combustion products depending primarily on the method of burning. Usually the SSL is burned in a reductive recovery boiler similar to a black liquor recovery boiler. Most of the inorganic dry solids are then transformed into a smelt of primarily Na_2S and Na_2CO_3. Part of the inorganic dry solids are entrained in the flue gases as Na_2SO_4. It, however, is efficiently recovered by electrostatic precipitators and returned to the furnace to be reduced to Na_2S. The dust emission, therefore, stays low and usually it is about 1 kg Na_2SO_4/t (2 lb Na_2SO_4/ton). The SO_2 emission may vary widely and is a function of the SSL sulfidity (5).

The treatment of the emissions from sodium SSL combustion depends on the particular chemicals recovery system chosen. At present there are 10 major sodium SSL chemical recovery systems with additional "customized" variations (IPC, Mead, Stora, Sivola, Western Precipitation, AST, SCA-Billerud, Tampella, ITT-Rayonier, and cross-recovery with a kraft mill). Both the CO_2 and SO_2 in the flue gases may be used, and depending on the system, SO_2 emissions will be about 6-20 kg SO_2/t (12-40 lb SO_2/ton).

Combustion under reducing conditions similar to the conditions in a black liquor recovery boiler, especially to those in a pyrolysis reactor (AST and SCA Billerud), will also produce H_2S. (H_2S generation and abatement in a black liquor recovery boiler were discussed in section 10.2.) H_2S from a pyrolysis reactor is usually converted to sulfur in a Claus reactor or oxidized to SO_2 in a separate furnace. H_2S emissions are negligible.

14.6 Acid Preparation Gases

Preparation of the cooking acid occurs in two steps, preparation of the raw acid and eventual fortification to cooking acid strength. With chemical recovery, raw acid preparation is simultaneously the recovery process. Acid preparation gases pose a minor SO_2 emission problem.

14.6.1 Calcium Cooking Acid Preparation

With calcium base, SO_2 derived from burning of sulfur or pyrite is passed countercurrently to water in towers packed with limestone (Figure 14-4). The vent to the atmosphere will emit some SO_2, but this emission is rather minor and usually amounts to less than 1 kg SO_2/t (2 lb SO_2/ton). Typical values are 0.2 kg SO_2/t (0.4 lb SO_2/ton) with a 20° C (68° F) water temperature (1, 8). Higher water temperatures might increase the emission of SO_2 by decreasing absorption efficiency.

The raw acid is fortified to cooking acid strength with digester relief and blowdown; the vent from the acid fortification system is connected to the acid tower (Figure 14-5).

14.6.2 Magnesium Cooking Acid Preparation

Magnesium raw acid is prepared in the chemicals recovery system (Figure 14-6). The raw acid may be used directly for bisulfite cooking or fortified for acid bisulfite cooking (Figure 14-5). In both cases, the only emissions will be with the flue gases from the chemicals recovery system. About 15 to 25 kg SO_2/t (30 to 50 lb SO_2/ton) will be emitted. This amount can be decreased by additional recovery stages.

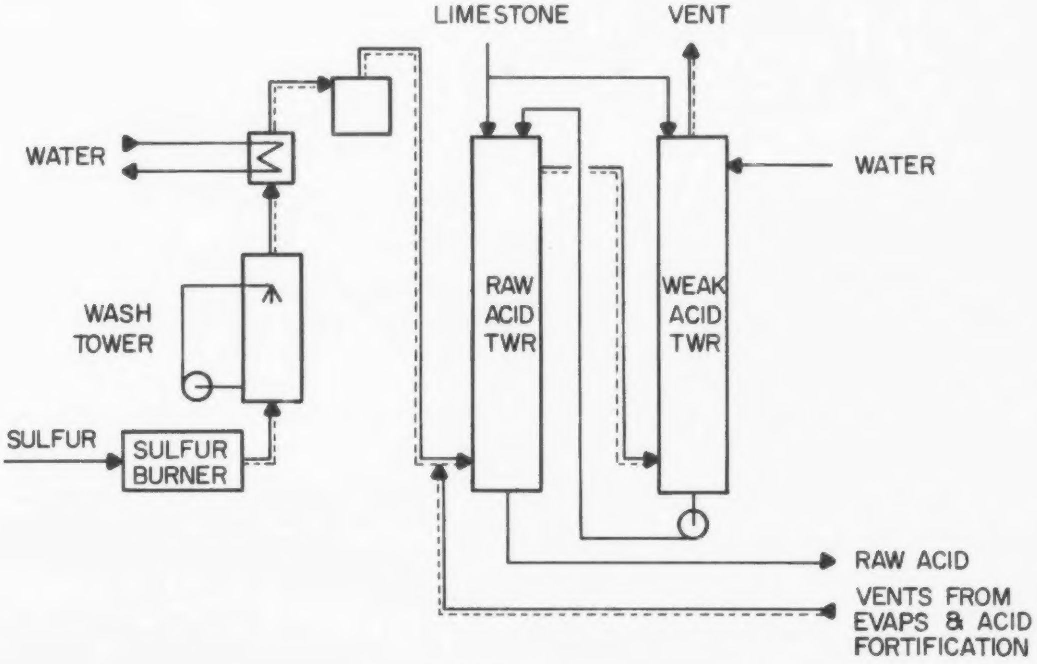
LIMESTONE
VENT
WATER
WATER
WASH
TOWER
RAW
ACID
TWR
WEAK
ACID
TWR
SULFUR
SULFUR
BURNER
RAW ACID
VENTS FROM
EVAPS & ACID
FORTIFICATION

FIGURE 14-4

FLOW SHEET FOR CALCIUM BASE RAW ACID PREPARATION

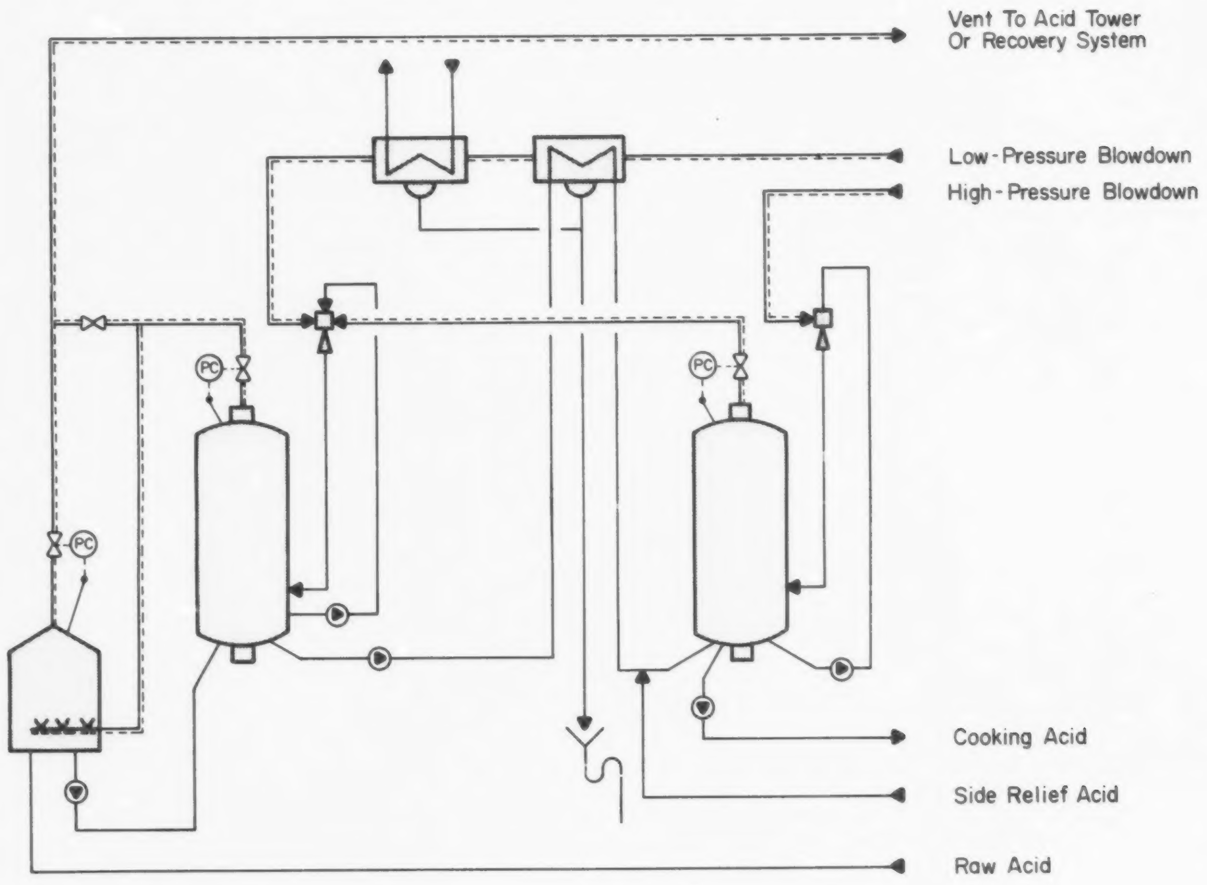
Vent To Acid Tower
Or Recovery System
Low-Pressure Blowdown
High-Pressure Blowdown
PC
PC
PC
Cooking Acid
Side Relief Acid
Raw Acid

FIGURE 14-5

ACID BISULFITE FORTIFICATION SYSTEM FLOW SHEET

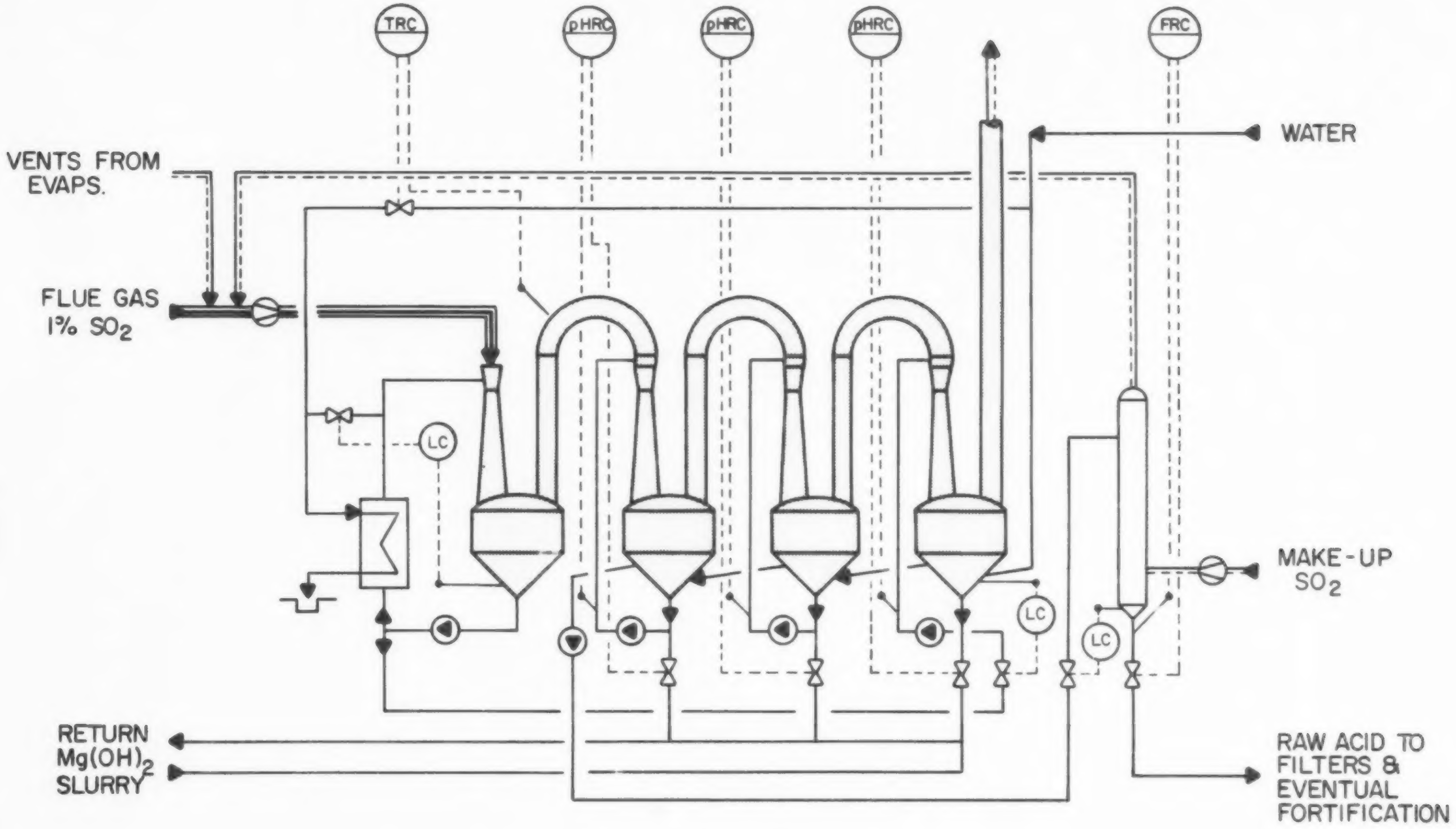
TRC
pHRC
pHRC
pHRC
FRC
WATER
VENTS FROM EVAPS.
FLUE GAS 1% SO_2
LC
LC
LC
MAKE-UP SO_2
RETURN
$Mg(OH)_2$ SLURRY
RAW ACID TO FILTERS & EVENTUAL FORTIFICATION

FIGURE 14-6

FLOW SHEET FOR MAGNESIUM BASE RAW ACID PREPARATION

14.6.3 Ammonium Cooking Acid Preparation

Ammonium cooking acid preparation systems are similar to those described above. Sulfur dioxide, either from sulfur burning or from flue gases, is absorbed in an NH_3 solution. Depending on pH, there is a potential for NH_3 emissions. Performance runs with spray tower absorbers using liquid circulation have shown that when the pH dropped below 6, almost 10 percent of the SO_2 feed was lost through the tower vent, while NH_3 losses were negligible. When the circulation pH rose above 7.6, NH_3 losses were substantial, but SO_2 losses went down to 0.3-0.6 percent. A pH of 7.1 kept both SO_2 and NH_3 losses below 1 percent, but caused a large plume from the absorption tower vent (1). Fine pH control is required to maintain SO_2 and NH_3 emissions at acceptable minimums.

14.6.4 Sodium Cooking Acid Preparation

There are as many systems for sodium cooking acid preparation as there are for sodium recovery. These recovery systems are covered in section 14.7.

14.7 SSL Recovery Boilers

14.7.1 Design Parameters

Spent sulfite liquor is, as a rule, incinerated to recover both heat and cooking chemicals in reusable form. Whenever chemicals are recovered, their recovery is considered the primary purpose of the incineration process, especially for magnesium- and sodium-based processes where the base is recovered. In the calcium-based process, recovery of the base is not feasible, and in the ammonium-based processes, only SO_2 can be recovered.

Since sodium bisulfite recovery was previously discussed under kraft processing, magnesia (MgO) recovery is discussed in this section.

There are a variety of SSL combustion systems. To help in evaluating different systems, a short survey of combustion fundamentals and requirements will be presented.

Burning intensity, which is the heat input rate per unit of furnace volume, depends mainly on temperature. The theoretical combustion temperature is a function of SSL heat value, combustion air temperature, and fuel-air ratio. The actual combustion temperature depends, in addition, on the heat and mass exchange with surrounding zones.

Stable ignition requires transport of energy to the ignition zone. This is normally accomplished by recirculation of hot furnace gases or hot air. The recirculation can be external or internal.

Complete combustion is essential for the recovery of chemicals and heat. A necessary condition for complete combustion is sufficient residence time in the high temperature zone of the furnace. This requires sufficient furnace volume and controlled flow pattern.

Since magnesium sulfate ($MgSO_4$) cannot be economically converted into magnesium bisulfite, a low sulfate content of the combustion product is important relative to recovery. The formation of sulfate depends on factors, such as combustion excess air, combustion temperature according to the chemical equilibrium, the residence time of the ash in intermediate temperature zones, and different catalysts. Not all sulfate formation mechanisms are fully understood.

Additional design parameters are set by requirements of boiler availability and controllability. Therefore, the most important factors become heat surface fouling and partial load combustion control.

14.7.2 SSL Recovery Boiler Systems

Burning of SSL is usually carried out in power-type boilers with some modifications. Ash-free auxiliary fuels can normally be burned in the same furnace or boiler without great disadvantage, if the auxiliary fuel input is not too high when compared to the SSL input. Possible disadvantages of using auxiliary fuel are dilution of the gases to the SO_2 recovery system and an increased percentage of sulfate due to temperature conditions and catalytic conversion. SSL boilers commonly have a low furnace heat release rate, which requires a low furnace exit temperature, widely spaced heat exchange surfaces, and effective heat surface cleaning equipment. Similar features exist in successful kraft recovery boiler designs.

SSL burning in a fluidized bed reactor was practiced, to some extent, for all soluble bases. This system is normally supplied as an integrated recovery unit and not in combination with a power boiler. Environmentally, it does not differ very much from a conventional recovery unit. The actual burning of SSL can be carried out in a variety of different burning systems. The most important systems are:

1. Small precombustion chambers, called Loddby furnaces;
2. Large furnaces, called Lurgi-Lenzing-Steinmuller (LLS);
3. Small furnaces of Babcock & Wilcox (B&W) for liquor burning;
4. Furnaces, designed by Tampella, that incorporate features of both LLS and Loddby furnaces; and
5. Fluidized bed reactors by Copeland and Dorr-Oliver.

Loddby furnaces are small precombustion chambers that are usually horizontal and are attached to a main boiler furnace. The refractory walls of the cylindrical chamber heat the tangentially-introduced combustion air to a high temperature. External recirculation stabilizes the flame in the muffle. The burnout of the flame occurs in the main furnace. The flame temperature at the muffle exit is approximately 175° C (350° F) below the theoretical combustion temperature. The dust from a Loddby furnace usually has a smaller mean particle size than dust from most other combustion systems. Loddby furnaces have good controllability and, if a few of these chambers are used jointly, they are suitable for partial load operations. In some Scandinavian mills, SSL is considered a good pressure control fuel for recovery-power boilers.

Lurgi-Lenzing-Steinmuller (LLS) furnaces are large units that are integrated with a steam boiler main furnace, but are separated by a verticle membrane tube wall that has a screen passage in the lowest part. Excess cooking of the furnace is prevented by covering the tube walls with a thin refractory layer. The LLS furnace exit temperature is about 305° C (550° F) below the theoretical combustion temperature. Effective ignition and mixing is accomplished by spraying the SSL countercurrently to the air flow.

Babcock & Wilcox furnaces for liquor burning are uncooled or slightly cooled. They can be similar to the LLS furnace. Unlike other systems, B&W uses self-stabilizing liquor burners that have their own air registers. Auxiliary fuel is burned in the same or in different burners. The controllability of a B&W system is good.

Tampella furnaces are combinations of LLS furnaces and Loddby furnaces. Only Ca-based liquor has been fired thus far.

Fluidized bed reactors, by Copeland and Dorr-Oliver, are used to some extent for SSL treatment. They provide an environment for combustion that gives a high intensity of reaction at comparatively low temperatures.

14.7.3 Operation Parameters

Because the recovery boiler is normally followed by chemical recovery, boiler operation has a greater direct influence on the chemical cycle than on the gas and solids emission from the plant.

Excess air and the use of auxiliary fuel, for an existing installation, are the most important operating parameters. The firing rate is also important, although large variations are not normally expected.

For calcium-base SSL without recovery, the excess air has little or no influence on the amount of SO_2 or SO_3 emitted from the boiler. High excess air can somewhat improve the formation of sulfate and, thus, reduce the amount of SO_2 and SO_3. Even a complete sulfatizing of the base will bind only about 65 percent of the sulfur. A normal value is about 35 percent. Using too much excess air can make heat recovery uneconomical.

The dust content of the flue gases from calcium-base SSL firing is often approximately 11.5 g/m^3 (5 gr/cu ft) when continuous sootblowing is practiced. With intermittent sootblowing, the concentration can be as low as 8-9.2 g/m^3 (3.5-4 gr/cu ft); during sootblowing, it is correspondingly higher.

The use of auxiliary fuel dilutes the flue gases to lower concentrations, but increases the costs of dust separation and eventual SO_2 removal. The use of wood refuse as fuel in the same boiler improves the binding of SO_2 and SO_3 to the ash.

Variation of excess air to Mg-base SSL liquor firing changes the sulfate content of the ash. Low excess air should be used to avoid sulfate formation so that all sulfur is converted to SO_2 in the flue gas for more efficient recovery. In practice, a part of the Mg, usually less than 10 percent, leaves the boiler as sulfate with a correspondingly slight decrease in the concentration of SO_2.

Only natural gas and oil can be used as auxiliary fuels. Even a high sulfur heating oil dilutes the flue gas SO_2 concentration, and no appreciable extra SO_2 absorption is expected from oil use. An excessive use of auxiliary fuel may increase the sulfatizing of the base or the formation of weakly soluble combinations.

Soot formation must be avoided, especially when burning auxilliary fuels. The soot will discolor the MgO ash and may also discolor the cooking acid made from the ash. Ultimately, the soot may discolor the pulp.

The operating parameters seem to have a great influence on the results of firing ammonia-based SSL. Different problems were reported, such as pluggage of boilers, boiler corrosion, and the emission of smoke, often referred to as blue haze. According to one mill plant, by installing and using glass fiber-bed demisters on an SO_2 absorption system (6), the blue haze is eliminated.

In tests by EKONO, the pH of the ash correlates strongly with the excess air of liquor burning. This correlation is probably caused by formation of SO_3 during the combustion. By combining ammonia-base SSL and bark-firing, an alkaline ash reaction with a low excess air is possible. Where sulfur recovery is not feasible, an alkaline ash is the only way to prevent SO_3 formation and subsequent direct discharges of it into the atmosphere.

14.8 SSL Recovery Systems

The combustion gases for bases that are feasibly recoverable are usually treated in a chemical recovery system. The efficiency of the recovery process is also an indication of the amount emissions. Because of high costs, SO_2 recovery has been limited to 50-80 percent and dust separation to 95-99 percent, both depending on the base and the recovery system. These recovery efficiencies, however, can be increased with higher investment. Dust emissions below 1 kg/t and SO_2 emissions below 10 kg SO_2/t (2 lb and 20 lb/ton, respectively) have been adopted as emission regulations for new sulfite mills (9, 10). These regulations will effectively phase out calcium-based sulfite mills in the future and will require more efficient recovery systems for the other bases.

All sodium recovery systems that displace H_2S from dissolved sulfide solutions with flue gas CO_2 or sodium bicarbonate ($NaHCO_3$) will have H_2S as an intermediate gas in the system. The H_2S is usually converted to sulfur in either a Claus reactor or oxidized to SO_2 in a furnace with almost 100 percent efficiency in both cases. Under normal circumstances, H_2S is not emitted into the atmosphere.

The recovery of soluble base chemicals and SO_2 is carried out using a few well known chemical reactions. Nevertheless, the number of systems offered is large. Also some plants use their own methods, which have not yet been described in the literature.

14.8.1 Magnesium Base

The basic reaction in all systems is an absorption of flue gas SO_2 into $Mg(OH)_2$ to produce a bisulfite solution.

In the B&W process (see Figure 14-7), the recovered MgO together with the make-up MgO is slaked with steam addition. The hydroxide is circulated in absorption venturis in countercurrent flow. The hydroxide reacts with recirculated $Mg(HSO_3)_2$ to form $MgSO_3$. In the recirculating acid, the sulfite reacts with SO_2 to form new $Mg(HSO_3)_2$. The extent of SO_2 absorption in each stage is governed by acid concentration, SO_2 concentration in the gas, temperature, recirculation rate, and gas velocity. The use of venturi absorbers has made much higher monosulfite concentration possible than produced with packed towers. Combustion gases discharged to the recovery system stack can be expected to contain less than 250 ppm SO_2 by volume.

The system as practiced in Veitsiluoto, Finland, has no dust separation and no separate slaking system. The initial circulation solution is formed in the first tower, somewhat simplifying the system. The design of the dust absorption system depends on close operational tolerances, but seems to work satisfactorily.

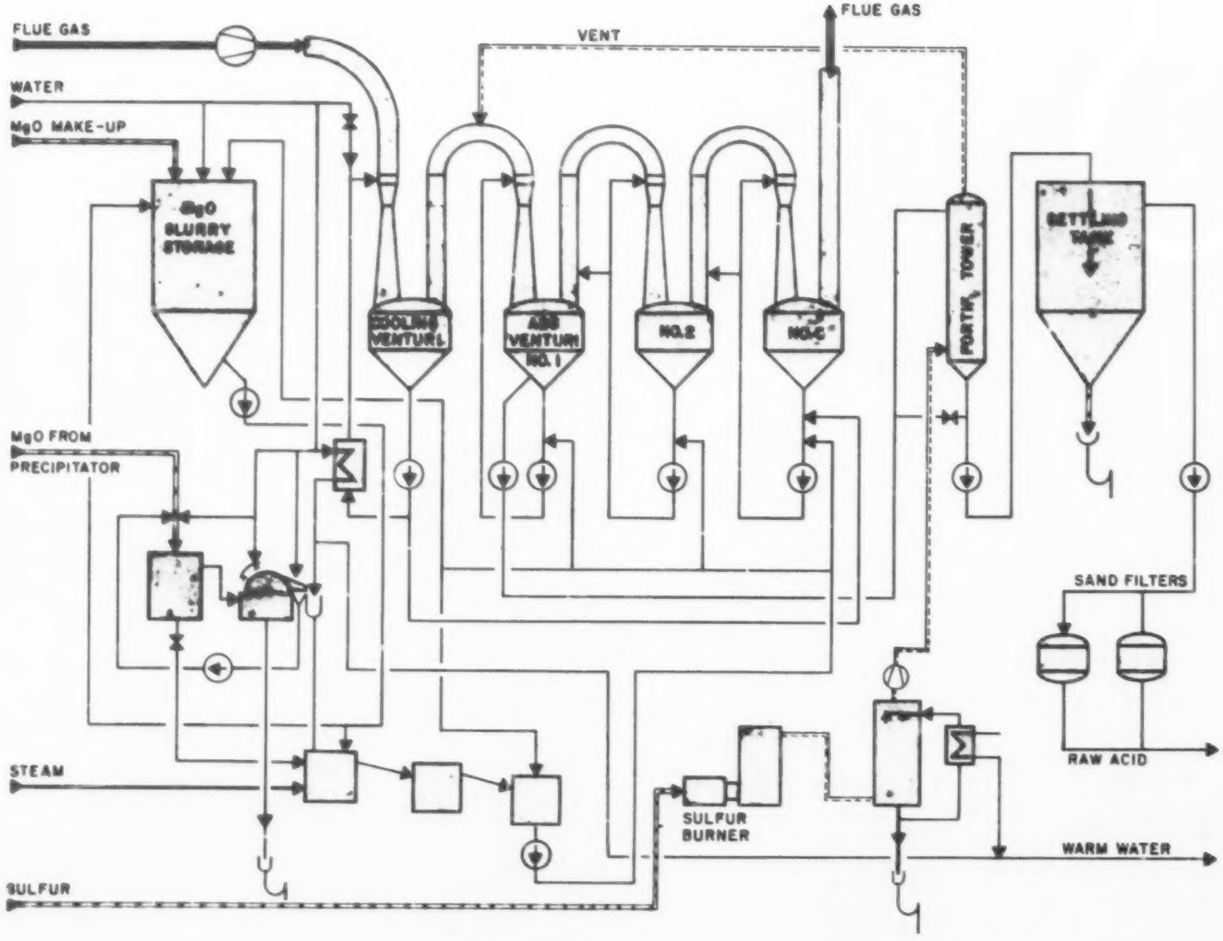
FLUE GAS
WATER
MgO MAKE-UP
MgO SLURRY STORAGE
VENT
FLUE GAS
COOLING VENTURI
ABS VENTURI NO. 1
NO.2
NO.C
FORTIF. TOWER
SETTLING TANK
MgO FROM PRECIPITATOR
SAND FILTERS
RAW ACID
STEAM
SULFUR BURNER
WARM WATER
SULFUR

FIGURE 14-7

BABCOCK & WILCOX PROCESS FOR MAGNESIA BASE SULFITE CHEMICALS RECOVERY

Systems with only one absorption unit have been offered by several manufacturers, among them Ahlström, Svenska Flaktfabriken, and Tampella. The reactors used are more complex, but can be considered as multistage reactors. Marbles have been introduced to increase the reaction surface, without significant effect.

In most cases, some heat is recovered from the gases in a cooling venturi before the absorption units.

The recovery plant stack is practically the only emission point. Excessive emissions of SO_2 usually occur only when the pH control of the absorption units does not work properly. High MgO emissions are normally the result of separator malfunction at plant overload.

14.8.2 Sodium Base

All recovery methods produce a solution of Na_2SO_3 or Na_2CO_3, or both, with the least possible concentration of undesired sulfur combinations. To obtain this result, the sulfur combinations are removed by carbonization with CO_2. The carbonate or bicarbonate is then converted to sulfite by sulfitizing with SO_2. In some processes the sulfides and bisulfides are removed by crystallization of the carbonate. A few modern recovery systems are:

1. The STORA process,
2. The SCA-Billerud process,
3. The Tampella process,
4. The Sivola-Lurgi process, and
5. The Institute of Paper Chemistry method.

In the STORA process, the clarified green liquor from the recovery boiler, containing Na_2S and Na_2CO_3, is carbonated with recirculated CO_2. Na_2S is converted to H_2S. The H_2S is stripped from the liquor by CO_2 as the carrier gas. The H_2S reacts in a Claus reactor with SO_2 to form elemental sulfur (S). The CO_2 is recirculated to the process. In this way the green liquor is converted to $NaHCO_3$. The $NaHCO_3$ is then reacted with $NaHSO_3$ to produce Na_2SO_3. Part of the sulfite solution absorbs SO_2 in an absorption tower and is returned as bisulfite.

Depending on process requirements, the cooking liquor is made from suitable proportions of the sulfite and bisulfite solutions. When a higher pH is needed as for semichemical pulping, some bicarbonate is bypassed to the sulfite solution. The principal process components of the STORA process are illustrated in Figure 14-8.

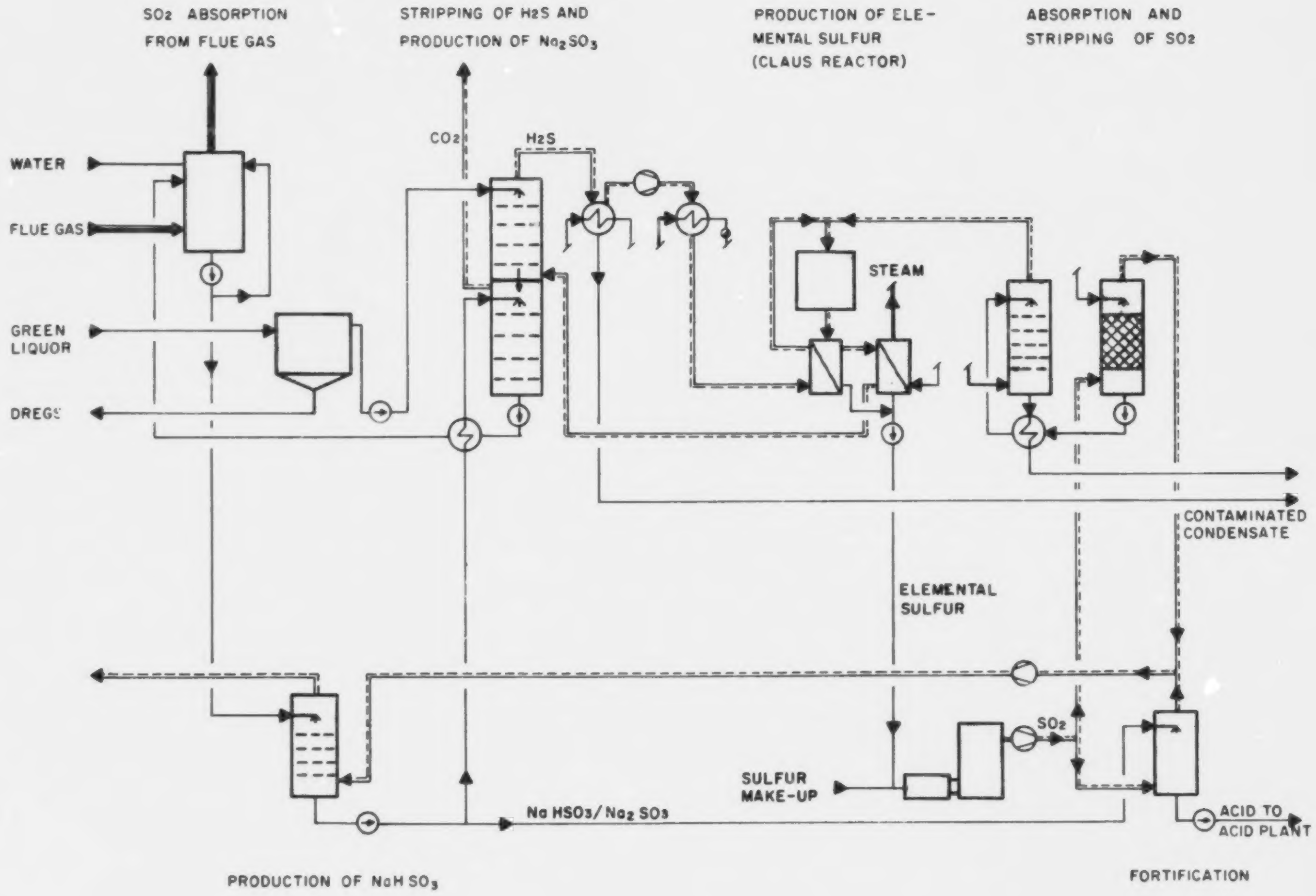
SO2 ABSORPTION FROM FLUE GAS
STRIPPING OF H2S AND PRODUCTION OF Na2SO3
PRODUCTION OF ELEMENTAL SULFUR (CLAUS REACTOR)
ABSORPTION AND STRIPPING OF SO2
WATER
FLUE GAS
GREEN LIQUOR
DREGS
CO2
H2S
STEAM
CONTAMINATED CONDENSATE
ELEMENTAL SULFUR
SO2
SULFUR MAKE-UP
Na HSO3/Na2 SO3
ACID TO ACID PLANT
PRODUCTION OF NaH SO3
FORTIFICATION

FIGURE 14-8

STORA PROCESS FOR SODIUM BASE SULFITE CHEMICALS RECOVERY

In the SCA-Billerud process, evaporated spent liquor is sprayed into a stream of hot combustion gases containing a small excess of air, but still insufficient for the combustion of the organic substances in the liquor. A pyrolysis of the liquors takes place, resulting in a combustible gas and a powder. The gas contains almost all the sulfur as H_2S, as well as other combustible components, including H_2, CO, and some hydrocarbons. The powder contains all the sodium, mostly as carbonate with a minor part as sulfate, as well as carbon. The process is illustrated in Figure 14-9.

The gas and powder mixture is cooled in a reactor boiler to a temperature well above the dew point of the gas, which produces high pressure steam. Separation of the powder from the gas occurs in both dry and wet separators. The gas is further cooled by condensing water vapor in a scrubbing tower, which enriches the gas before burning. The H_2S in the pyrolysis gases is converted to SO_2 in a boiler. The SO_2 in the flue gases is then absorbed by a soda lye solution before being exhausted.

The powder separated from the gas is mixed with water, and the soluble salts are leached out to produce the Na_2CO_3 solution used in the absorption just described. The remaining carbon can be burned separately.

To produce cooking liquor, the product from the SO_2 absorption is fortified with makeup sodium and sulfur in the acid making plant.

Like the STORA process, the Tampella process (Figure 14-10) is very flexible and can be applied to various cooking methods. The essential part of the Tampella process consists of three subprocesses: precarbonation, bicarbonation-crystallization evaporation, and preparation of bicarbonate by carbonation. The starting point is combustion of the black liquor in a reducing atmosphere. In the Tampella recovery process, a smelt consisting mostly of Na_2S and Na_2CO_3 is formed in a conventional way.

The smelt is dissolved in a strong green liquor, which, depending on the need, can be converted to H_2S, a high sulfidity smelt solution, a low sulfidity smelt solution, an Na_2CO_3 solution, or monohydrate crystals free from sulfide and thiosulfate. The H_2S can be burned to SO_2 for the preparation of Na_2SO_3 solution, or converted, by means of the Claus Process, to elementary S for the production of polysulfide liquor (11).

To prepare polysulfide liquor, a high sulfidity solution (88-92 percent) can be used by combining evaporation and mechanical separation of carbonate crystals. Low sulfidity carbonate solution can be used for preparing NSSC liquor or kraft white liquor. Crystal Na_2CO_3 can be employed for the neutralization of sulfite and black liquor and also for preparing low-yield Na_2SO_3 cooking liquor.

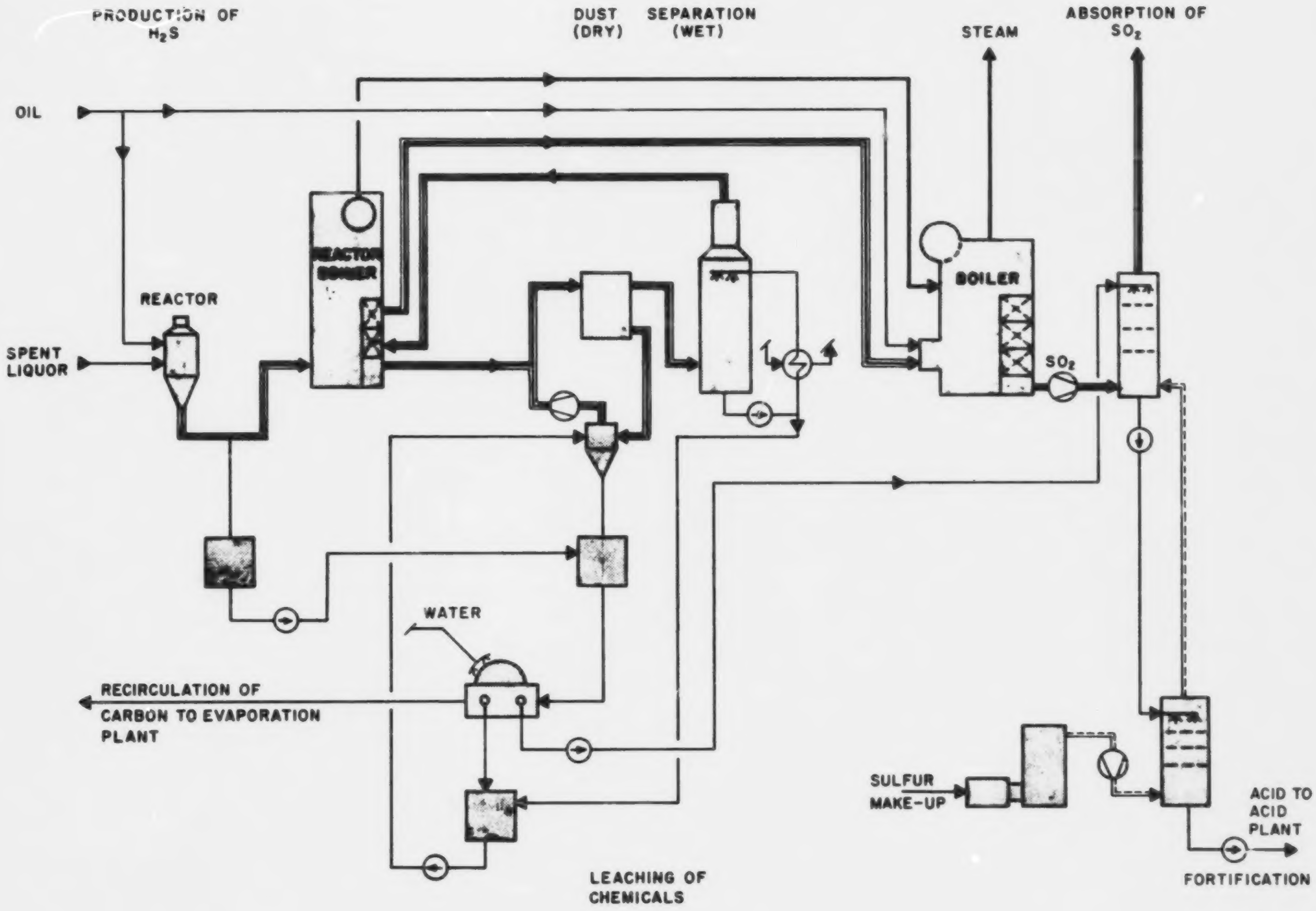
PRODUCTION OF H_2S
DUST (DRY)
SEPARATION (WET)
STEAM
ABSORPTION OF SO_2
OIL
SPENT LIQUOR
REACTOR
REACTOR BOILER
BOILER
SO_2
WATER
RECIRCULATION OF CARBON TO EVAPORATION PLANT
SULFUR MAKE-UP
ACID TO ACID PLANT
FORTIFICATION
LEACHING OF CHEMICALS

FIGURE 14-9

SCA PROCESS FOR SODIUM BASE SULFITE CHEMICALS RECOVERY

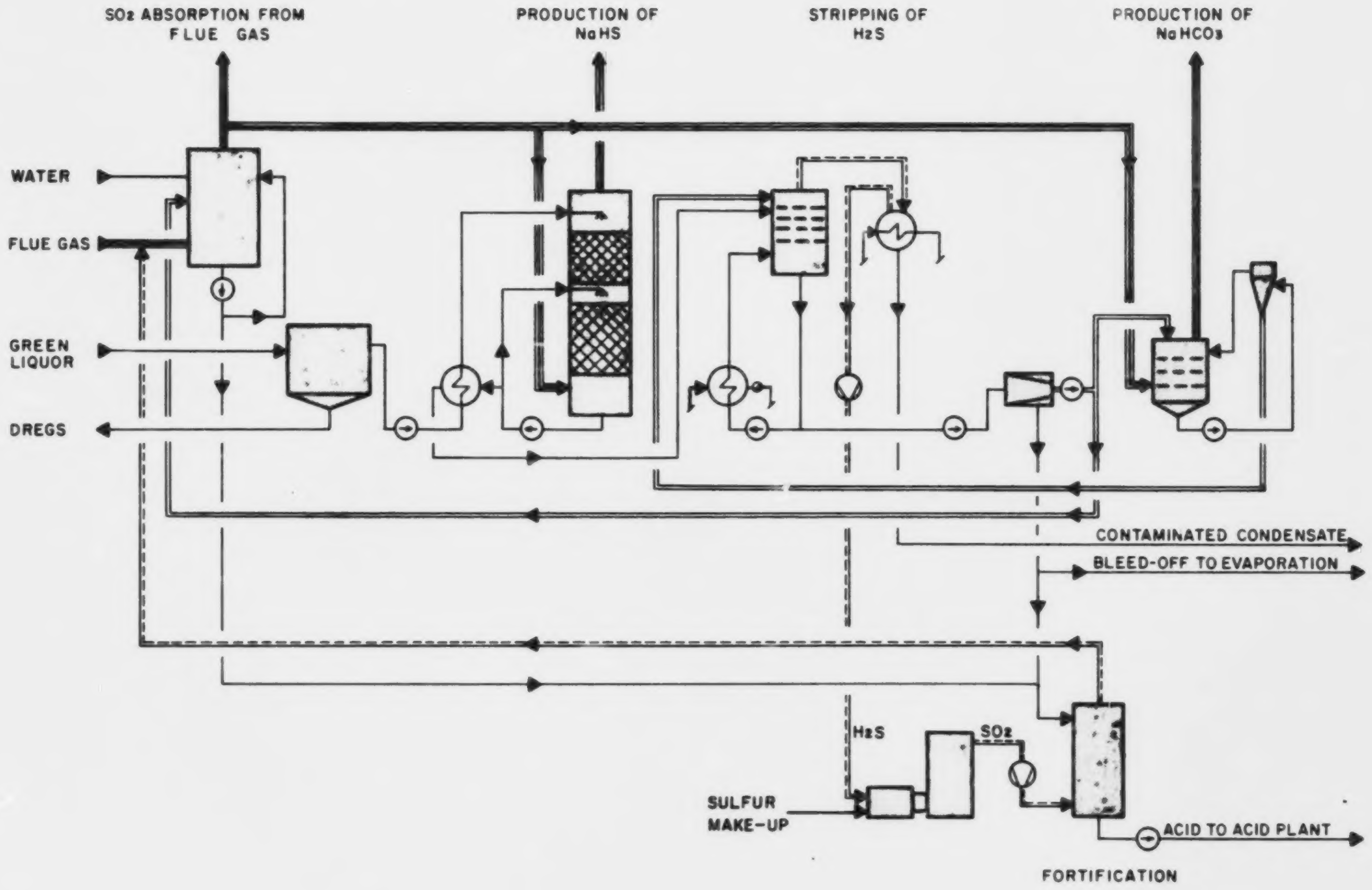
SO$_2$ ABSORPTION FROM FLUE GAS
PRODUCTION OF NaHS
STRIPPING OF H$_2$S
PRODUCTION OF NaHCO$_3$
WATER
FLUE GAS
GREEN LIQUOR
DREGS
CONTAMINATED CONDENSATE
BLEED-OFF TO EVAPORATION
H$_2$S
SO$_2$
SULFUR MAKE-UP
ACID TO ACID PLANT
FORTIFICATION

FIGURE 14-10

TAMPELLA PROCESS FOR SODIUM BASE SULFITE CHEMICALS RECOVERY

In the Sivola-Lurgi process, green liquor, containing mainly Na_2S and Na_2CO_3, reacts first in the precarbonation tower with the flue gases from the recovery boiler and then with CO_2 in the main carbonation stage. The purpose is to convert the active sodium of the green liquor to $NaHCO_3$ and to liberate the sulfide as H_2S in the carbonation stage. The bicarbonate obtained is then split thermally in a decomposer, producing Na_2CO_3 and CO_2 for carbonation.

The major portion of the carbonate reacts with $NaHSO_3$ in a reactor and produces Na_2SO_3 and CO_2. The reactor and the decomposer are built one above the other and connected with a clock bottom. Portions of the Na_2SO_3 obtained are used for cooking liquor preparation and for sulfitation. In sulfitation step Na_2SO_3 reacts with SO_2 to produce bisulfite. The SO_2 is obtained by burning elementary sulfur and H_2S in the same furnace.

The method of the Institute of Paper Chemistry is probably the simplest. On the other hand, the products of the reaction can be controlled only within certain limits. The green liquor is piped after clarification to the sulfitation tower, where it is treated with SO_2 from a sulfur furnace. The formation of thiosulfate cannot be prevented, but it can be kept at a reasonable level, 7-15 percent in the cooking liquor. The Na_2SO_4 content can be kept below 5 percent. As a final product, a mixture of Na_2CO_3 and Na_2SO_3 is obtained, which, after makeup, can be reused in the NSSC process.

14.8.3 Ammonium Base

Since this base cannot be recovered, recovery is limited to SO_2. SO_2 recovery can take place in the same type of equipment as for the magnesium base. For the operation of a multistage venturi absorber system, pH control is essential for proper functioning (see section 14.7.3).

14.9 Problem of Nitrogen Compounds from Ammonium-Based Pulping

Ammonium base SSL contains about 3 to 10 percent N_2 by weight on a dry solids basis (11). Nitrogen in spent sulfite liquor is present primarily in the form of ammonium salts, which can result in the emission of ammonium sulfite and ammonium sulfate containing particles from the recovery furnace. The gaseous forms of N_2 that can be emitted from the recovery furnace include diatomic nitrogen gas (N_2), NH_3, and nitrogen oxides. Amine compounds can theoretically be emitted from the ammonium-base sulfite recovery furnace, particularly in strongly reducing atmospheres.

Variables affecting the generation and relative amounts of the respective individual nitrogen compounds which can be formed include the nitrogen content of the fuel, the flame temperature, the flame zone retention time, and the configuration of the combustion unit.

The flame temperature is influenced by the heating value of the fuel, the moisture content, the heat release rate, and the combustion volume of the furnace.

Blakeslee and Burbach (12) report that nitrogen oxide emissions tend to increase with the nitrogen content for the coal- and oil-fired power boilers. Little information is available regarding the effect of the fuel nitrogen content of ammonium base SSL; however, there are indications that at the lower flame temperatures, particularly below 1200° C (2200° F), the primary gaseous products are N_2 and NH_3. The nitrogen present in the fuel is not present in the diatomic elemental form, but as NH_4 ion.

Flame temperature is an important variable affecting the relative amount of nitrogen oxide emissions formed during the combustion of SSL. Palmrose and Hull (13) report that the flame temperature during ammonium base SSL combustion is about 980 to 1315° C (1800 to 2400° F). The flame temperature is observed to increase as the solids content of the spent liquor increases, because less water is present from the fuel being evaporated to act as a heat sink. Heat release rates for ammonium base sulfite recovery furnaces generally are about 1.9 to 8.8 GJ/h per cubic meter (50,000 to 230,000 BTU/hr per cubic foot) (14). Heating values are generally between 16 and 21 MJ per kg of dry solids (7,000 to 9,000 BTU/lb). Loddby-type furnaces normally have relatively large combustion volumes so that excessively high temperatures are not found when burning ammonium base SSL.

Studies by Bartok, Crawford, and Skopp (15) indicate the effect of fuel nitrogen content on nitrogen oxide emissions. Tests run on fuel oil-fired power boilers indicate that the amount of No formed is directly proportional to the nitrogen content of the fuel over a range of 0.2 to 1.0 percent nitrogen by weight. The nitrogen content of the fuel appears to be the predominant factor affecting NO emissions at temperatures below 1300° C (2370° F). Flame temperature appears to be the predominant factor affecting NO formation above 1100° C (2000° F), particularly at O_2 concentrations above 2.0 percent by volume in the flue gas.

Because of the lower nitrogen content of fuel oil (0.2 to 1.0 percent by weight) compared to ammonium base SSL (3.0 to 10.0 percent by weight), the results of the Bartok *et al.* study are not directly applicable to recovery furnaces. They do tend to indicate the general trend of increasing NO emissions in direct proportion to fuel nitrogen content. This relationship is applicable particularly at the lower flame temperatures observed in ammonium base sulfite recovery furnaces because of the large combustion volumes and the high moisture contents of the fuels.

A very limited amount of measurements have been made regarding NO emissions for ammonium base sulfite recovery furnaces. Results of one series of tests indicate that total nitrogen oxide concentrations ranged from 200 to 500 ppm by volume as NO_2 with peak values observed of up to 1000 ppm (16). A summary of results is presented in Table 14-5.

TABLE 14-5
NITROGEN OXIDES* EMISSIONS FROM AN AMMONIUM BASE SULFITE RECOVERY FURNACE (16)

	Concentration	Emission Rate**			
Condition	ppm by volume	kg NO_x/t	(lb/ton)	kg $NO_x/10^6$ kJ	(lb $NO_x/10^6$ BTU)
Average	350	8.3	(16.6)	0.36	(0.84)
Minimum	200	4.7	(9.4)	0.22	(0.51)
Maximum	500	11.8	(23.6)	0.52	(1.21)

*Nitrogen oxides are computed as equivalent nitrogen dioxides.

**Based on flow rate 625 m^3/h per daily metric ton of capacity (24,300 ft^3/h per short ton) and a liquor heating value of 22.7 MJ/kg (9750 BTU/lb).

Concentrations as reported are substantially greater than the 25 to 75 ppm of NO_x for kraft and magnesium base sulfite recovery furnaces, indicating the possible role of nitrogen content of the fuel in causing NO_x emissions.

Nitrogen oxide emissions can be controlled by one or any combination of the following methods:

1. Evaporating to the minimum solids content (about 50 percent) necessary to support combustion and to provide efficient heat recovery, with the remaining water acting as a heat sink during combustion;

2. Operating furnaces at relatively low firing rates to minimize the rate of heat release;

3. Modifying the type of combustion unit in which the SSL is burned, as by shifting to the use of fluidized beds; and

4. Operating the furnace at minimum excess air consistent with efficient combustion in an oxidizing atmosphere.

It is also possible to reduce the nitrogen content of the fuel by reducing the amount of NH_3 added to the chemical makeup. The effect would be to reduce both the NH_3 and nitrogen oxide emissions from the combustion process. The NH_3 produced could be removed in the acidic scrubbing solution during passage through the series of liquid scrubbers. The danger in reducing the NH_3 makeup is that it could alter the pulping conditions adversely and reduce the pH of the liquid scrubbing solution, resulting in increased emissions of SO_2.

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CHAPTER 15

OTHER PROCESS SOURCES

15.1 Bleach Plant Gases

Bleach plant gases differ significantly from other gaseous emissions from a kraft mill. Depending on the bleaching system and the bleach chemical preparation, the gaseous effluents may include Cl_2, chlorine dioxide (ClO_2), and SO_2. All of these gases have about the same odor threshold of about 0.1-1 ppm. The bleach plant belongs to the minor air pollution sources in a kraft mill; its influence is usually restricted to the mill area itself or to the immediate surroundings. The noticeable effects of the bleach plant gaseous emissions are mainly odor and corrosion of nearby objects.

15.1.1 Bleach Plant Cl_2 Emissions

If a bleach plant has a chlorination stage, there are Cl_2 emissions from the Cl_2 bleach tower vent and from the hood vent of the succeeding washing stage. If the washer is of a vacuum rotary drum type, the total Cl_2 emission is about 0.5 kg Cl_2 per metric ton of pulp (1 lb Cl_2/ton) and the total vent flow is about 900 m^3/t (29,000 ft^3/ton) (1).

For a pressure filter or a continuous diffuser, the vent gas flow is much smaller and more concentrated in Cl_2. The Cl_2 emission is much smaller, too. One feasible way of eliminating the Cl_2 emission is to scrub the Cl_2-containing gases with an NaOH solution. This, in turn, can be used as a part of the hypochlorite solution needed in the hypochlorite bleaching stage. By eliminating Cl_2 emissions, Cl_2 is saved. Profits are based on Cl_2 savings and on scrubber investment and operational costs.

15.1.2 Bleach Plant ClO_2 Emissions

If the bleach plant has two ClO_2 stages, ClO_2 is emitted from both the washer hood vents after the bleach towers and the ClO_2 manufacturing process itself.

If the washers are of a vacuum rotary drum type, the total ClO_2 emission is about 0.3 kg ClO_2/t (0.6 lb ClO_2/ton) and the corresponding vent flow is approximately 800 m^3/t (26,000 cu ft/ton) (1). Pressure washers or continuous diffusers will give smaller flows and emissions.

The washer hood vent gases are too diluted for ClO_2 recovery. Therefore, ClO_2 destruction through scrubbing with an alkaline hydrogen peroxide (H_2O_2) solution is the only feasible treatment. The reaction is:

$$2\,ClO_2 + 2\,NaOH + H_2O_2 = 2\,NaClO_2 + O_2 + 2\,H_2O$$

The sodium chlorite ($NaClO_2$) solution must be eliminated with the mill wastewaters, since oxidation to ClO_2 with Cl_2 is hardly feasible. The H_2O_2 is expensive, and yearly scrubbing costs may amount to almost 30 percent of the scrubber investment.

In every ClO_2 manufacturing process, the last step consists of an absorption stage where the ClO_2 gas is run countercurrently to a stream of cool water to produce a ClO_2 solution. The ClO_2 concentration is usually between 5 and 10 g/l. The ClO_2 loss or emission from this absorption tower is directly proportional to the water temperature (Figure 15-1). At a water temperature of 20° C (68° F), the ClO_2 emission is about 0.2 kg ClO_2/t (0.4 lb ClO_2/ton) and the tower vent flow is about 60 m^3/t (1900 ft^3/ton) (1).

In warm climates, where the fresh water temperature is approximately 20° C (68° F), it may be feasible to recover more ClO_2 in the absorption tower simply by cooling the water. Cooling the water from 20° C (68° F) to 4° C (39° F) will decrease the ClO_2 emission from the absorption tower by 50 percent (Figure 15-1). In a colder climate, as in Canada or Scandinavia, cooling is not feasible. Here, alkaline H_2O_2 scrubbing must be used.

15.1.3 Bleach Plant SO_2 Emissions

A bleach plant may need SO_2 in either of two situations:

1. If it has a Mathieson process for ClO_2 manufacture, or

2. If it has a final SO_2 treatment stage (to destroy Cl_2 and hypochlorite rests and to adjust the pH of the pulp).

This treatment requires an absorption tower for manufacturing SO_2 water, and the tower will emit some SO_2. Gas flows are probably about 25 m^3/t (800 ft^3/ton) and the SO_2 emission is approximately 1.5 kg SO_2/t (3 lb/ton) (1).

In warm climates, SO_2 recovery through cooling of the fresh water may be possible. Reducing the fresh water temperature from 20° C (68° F) to 4° C (39° F) will decrease the SO_2 emission by 75 percent (Figure 15-2).

In colder climates, fresh water cooling is not feasible. Tower vent gases may be scrubbed with an alkaline solution in combination with Cl_2 emissions from the bleach plant, but then the Cl_2 is no longer recovered as hypochlorite (section 15.1.1).

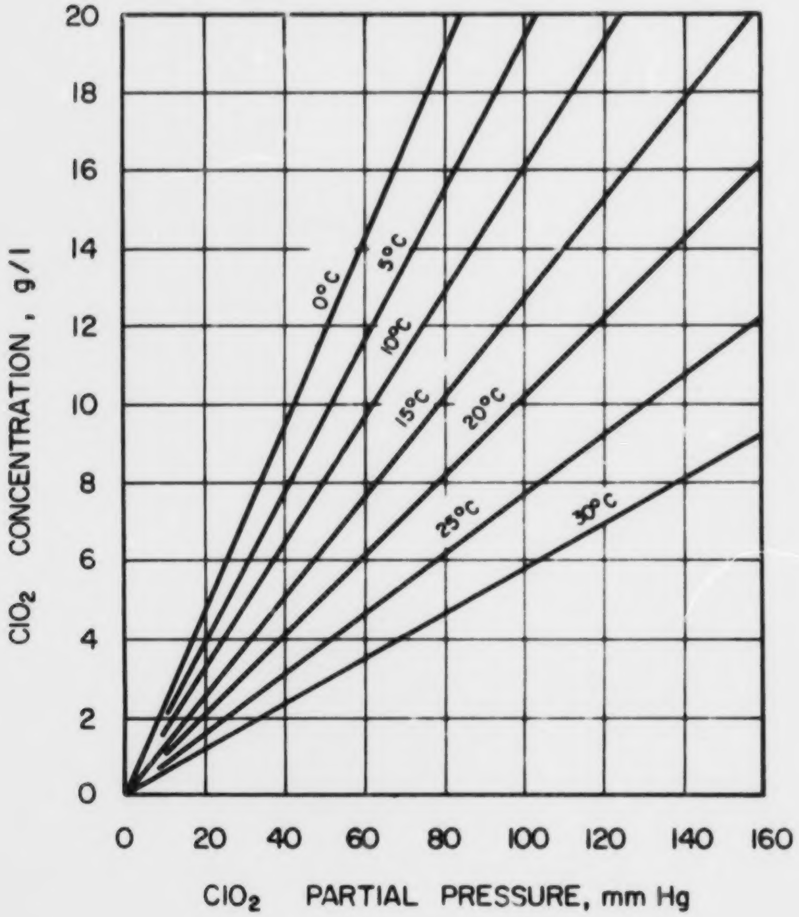

FIGURE 15-1
EQUILIBRIUM SOLUBILITY OF CHLORINE DIOXIDE IN WATER (2)

15.2 Wastewater Treatment

15.2.1 Process Variables

Release of malodorous gases from liquid effluent streams during transport or wastewater treatment operations has been frequently overlooked as an air pollution source. The major sources of odorous gases in liquid effluent streams are from the digester and evaporator condensate waters, with additional contributions from black liquor spills. Odorous gases can be released to the atmosphere from free liquid surfaces during open channel flow, from manholes and sewer vents (particularly if there is a change in liquid elevation), from pumping stations, from liquid recycling, and from wastewater treatment operations (4).

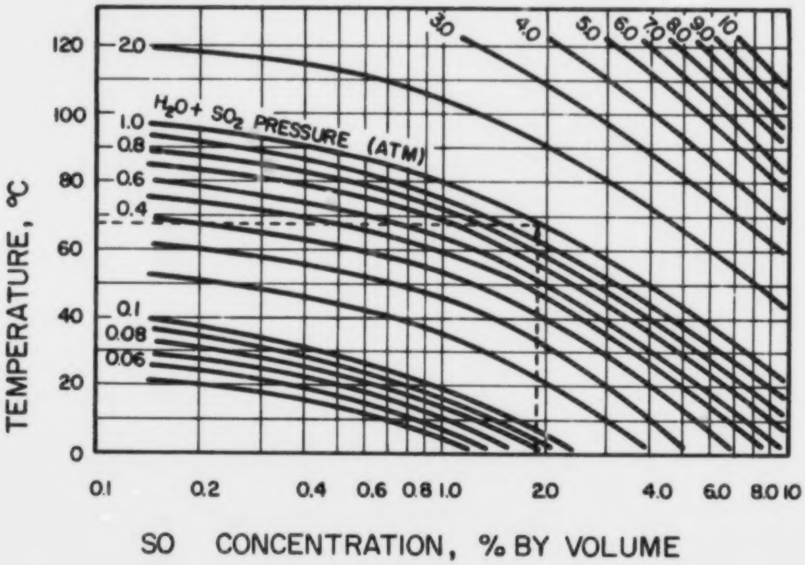

FIGURE 15-2

EQUILIBRIUM SOLUBILITY OF SULFUR DIOXIDE IN WATER (3)

The major physical and chemical processes that can result in evolution of odorous gases from liquid effluent streams include:

1. Volatilizing of dissolved gases by increasing liquid temperature;

2. Increasing the degree of liquid turbulence by agitation, pumping, or other means; and

3. Releasing acidic gases, such as H_2S and CH_3SH, by a reduction in liquid pH.

Specific processes that can result in increased evolution of odorous gases from wastewater streams include:

1. Contact with hot flue gas streams, as during liquid scrubbing;

2. Liquid pH changes resulting from contact with acidic flue gas streams containing CO_2, acidic liquids such as chlorination effluent waters, or spent acid streams from tall oil acidulation or ClO_2 manufacture; and

3. Agitation of liquid streams by mechanical aeration, diffuser aeration with gases, or other means.

Process variables affecting odorous gas release include inlet concentrations of the particular constituents, liquid temperature, pH changes, degree of agitation, physical configurations, O_2 content of the liquid, and biological activity.

The major chemical constituents that produce odors from pulp and paper mill effluent waters are organic sulfur and organic nonsulfur compounds. A major potential problem can exist with kraft pulp mills, where organic sulfur compounds, such as CH_3SH and CH_3SCH_3 formed during the cooking operations, can be released into digester condensate waters. They can also be released to a lesser extent from black liquor into evaporator condensate waters or from black liquor spills from storage tanks or overloaded multiple-effect evaporator systems.

Organic nonsulfur compounds, such as terpenes and other wood extractive materials, can also be evolved from effluent waters in either kraft or sulfite pulp mills. Terpene compounds can be evolved from digester condensate waters in kraft pulp mills in the form of droplets that can absorb sulfur gases from subsequent transport downwind from treatment processes. Overloaded or incompletely mixed biological waste treatment facilities with sludge accumulations or sections with inadequate dissolved oxygen (DO) levels can be the source of odorous gases, such as organic acids formed by anaerobic fermentation. Agitation of liquids, where these conditions exist, can result in the liberation of substantial quantities of malodorous gases to the atmosphere. If these gases are associated with particulate matter, such as bacterial cells or liquid droplets, they can be transported for long distances downwind.

15.2.2 Treatment Methods

The two major approaches to minimize malodorous gas generated from liquid effluent streams are by inplant treatment and by modification of the wastewater treatment facilities. The major inplant treatment methods to reduce odorous gas release to the liquid effluents are by air or steam stripping of digester and evaporator condensate waters. (These methods are discussed in Chapter 5 of the manual for kraft pulp mills and Chapter 14 for sulfite pulp mills.) An additional inplant treatment method involves effective housekeeping to minimize black liquor spills, as well as other spills, by accidents or carelessness, systems for segregation and containment of spilled liquids, and enclosure of flowing liquid effluent streams.

One step that can be taken to prevent release of odorous gases from effluent waters is to enclose tanks, as well as the biological aeration process. This step is feasible for activated sludge aeration processes, that it would normally involve a prohibitive expense if applied to aerated stabilization basins, because of the extensive surface areas involved. A modification to the activated sludge process was recently developed that employs molecular oxygen (O_2) as the oxygen supply and uses four enclosed aeration tanks in series (5). The system results in a small O_2-rich gas stream that is easily incinerated in a lime kiln or other combustion unit. The process also has potential as a pretreatment system, which is upstream of a conventional aerated stabilization basin, to biologically oxidize or stabilize rapidly reactive materials, such as terpenes or organic sulfur compounds.

Addition of specific oxidizing gases to the liquid stream will reduce odor levels in pulp and paper mill effluent waters. Gases that have possible application for deodorization of liquid effluent waters include Cl_2, ClO_2, O_2, and ozone (O_3). Alferova, Panova, and Titova (6) describe a two-stage system, developed in the Soviet Union, for treatment of digester and evaporator condensate waters by aeration and chlorination in series. The combined condensate liquid is first aerated in a multiple tray tower with air and then contacted with acidic chlorination bleachery effluent for further oxidation of the odorous compounds present. Chlorine dioxide has been applied for effluent treatment odor control in the petroleum industry, and can have application in the pulp and paper industry (7).

The O_2 can also be used for odor control by augmenting dissolved oxygen levels in existing secondary wastewater treatment facilities. Murray and Rayner (8) report that CH_3SH is easily oxidized in the presence of O_2 to CH_3SSCH_3. The CH_3SSCH_3 can then be oxidized to sulfones, sulfonic acids, and other relatively innocuous products, but long retention times are required. Any CH_3SCH_3 is not easily oxidized in the presence of O_2 except at very high temperatures not normally found in wastewater treatment.

Two recent studies describe the effects of O_2 addition to liquid effluent streams for augmenting dissolved oxygen levels in aerated stabilization basins and receiving waters. A sidestream oxygenation system installed at the Brewton, Alabama, kraft pulp mill, where 4.5 t (5 tons) O_2/day were added to the liquid effluent, resulted in an increase in dissolved oxygen levels and a decrease in odor from the aerated stabilization basin (9). Amberg (10) describes similar results when sidestream oxygenation is employed for augmenting dissolved oxygen levels in receiving waters.

15.3 Odor Problems from Diffuse Sources

A complete inventory of the odorous emissions from a kraft pulp mill has, so far, comprised measurements in stacks and other point sources only. In addition, however, odorous sulfur compounds are emitted from sources of a diffuse nature, such as leaking process equipment and settling basins; these must also be taken into account. Expansion of odor elimination systems for large point sources will increase the relative importance of the diffuse sources. A method for quantitative assessment of these emissions was developed and is described as follows (11):

1. The method uses simultaneous sampling and flow measurement in a suitable number of sections on the lee side of the diffuse source. The

total emission is calculated by summation of the contributions from individual sections.

2. The instrumentation consists of a fixed analysis unit (a gas chromatograph with a flamephotometric detector) and portable units that are all capable of simultaneous gas sampling and flow measurement.

The method was tested at a kraft pulp mill in a survey of the diffuse emissions from the settling basin, as well as from the digestery, recovery furnace, and limewashing building. The results of the measurements are given in Table 15-1.

TABLE 15-1
ODOROUS GASES FROM DIFFUSE KRAFT PULP MILL SOURCES (11)

	Emitted Compound-Emission Rate			
Diffuse Emission Source	H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3
	g/h (lb/hr)			
Settling Basin Measurement I	1,900 (4.2)	600 (1.3)	60 (0.13)	400 (0.88)
Settling Basin Measurement II	1,700 (3.8)	600 (1.3)	70 (0.15)	400 (0.88)
Settling Basin Measurement III	1,800 (9.0)	600 (1.3)	80 (0.18)	600 (1.3)
Digestery I (fir)	2 (0.004)	10 (0.022)	60 (0.13)	40 (0.088)
Digestery II (birch)	3 (0.007)	10 (0.022)	40 (0.088)	20 (0.044)
Recovery furnace I	4 (0.009)	10 (0.022)	10 (0.022)	30 (0.066)
Recovery furnace II	10 (0.022)	40 (0.088)	20 (0.044)	60 (0.13)
Limewash building	1 (0.002)	–	–	–

15.4 References

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CHAPTER 16

POWER BOILERS

16.1 Supply Patterns

The pulp and paper industry is a major energy consumer in the United States with a total process energy consumption requirement in 1970 of about 1.6×10^{18} J per year (1.5×10^{15} BTU per year). (See Chapter 1.) Based on 1972 figures compiled by the American Paper Institute, about 33 percent of the industry's total energy requirement is supplied by combustion of its waste pulping liquors and an additional 7 percent by combustion of wastewood and bark. The remaining 60 percent of the total energy requirement must be supplied by purchase of auxiliary fossil fuels, such as coal, oil, and natural gas or by purchase of electricity. A breakdown of the total national process energy supply patterns for the pulp and paper industry is presented in Table 16-1 (1). Considerable variations in energy supply for mills in different regions of the United States can exist.

TABLE 16-1
OVERALL NATIONAL DISTRIBUTION OF ENERGY SOURCES FOR THE PULP AND PAPER INDUSTRY (1) (2)

Energy Source	Overall Energy Consumption		
	% of Total*	MJ/yr**	(BTU/yr)**
Pulping liquors	33	522×10^9	$(495) \times 10^{12}$
Waste wood	7	110×10^9	$(105) \times 10^{12}$
Bituminous coal	11	174×10^9	$(165) \times 10^{12}$
Residual fuel oil	20	317×10^9	$(300) \times 10^{12}$
Distillate fuel oil	2	32×10^9	$(30) \times 10^{12}$
Natural gas	21	332×10^9	$(315) \times 10^{12}$
Purchased electricity	5	79×10^9	$(75) \times 10^{12}$
Other sources	1	16×10^9	$(15) \times 10^{12}$
Total	100	1582×10^9	$(1500) \times 10^{12}$

*Based on 1972 data.
**Based on 1970 data.

16.2 Combustion Parameters

To obtain usable energy from fuel, fuel is normally burned in air to release heat and then the heat energy is harnessed by using it to generate steam. The kinetic and thermal energy of the steam, in turn, can be used in any variety of ways. To make the fuel burn satisfactorily, it must be mixed with air in the proper proportions in a suitable furnace. To convert water to steam at appropriate pressure, the water normally flows through tubes, which are warmed on their outside by the hot gaseous products of combustion. Once steam forms, it is further heated to the desired degree of superheat by channeling it through another set of similar tubes, called the superheater. The types and amounts of air pollutants emitted from the combustion process depend on the characteristics of the fuel burned, the configuration of the combustion unit, and the operating parameters of fuel and air supply.

16.2.1 Fuel Characteristics

The major parameters affecting air pollutant formation during fuel combustion in power boilers are the physical state, heating value and moisture content of the fuel, as well as its ash, sulfur, and nitrogen contents. Coal and wastewood are the primary types of solid fuels employed; both require extensive materials handling facilities for the unburned fuel before combustion and for the noncombustible ash following combustion. Both distillate and residual liquid fuel oils are employed in the pulp and paper industry. Heavy residual fuel oil is more commonly used and has a high air pollution potential. Natural gas is the primary gaseous fuel employed in the pulp and paper industry; it is easiest to burn and has the lowest air pollution potential of all the fuels. Each of the different fuels requires a different type of combustion unit because of differences in burning characteristics.

The heating value of a fuel determines the amount that must be burned to generate a given amount of usable energy. The heating value varies with the kind of fuel employed, the location from which it was derived, and its moisture content. Heating values for bituminous coal and wastewood can vary substantially among those derived from different locations, as can their ash and sulfur contents. A summary of typical heating values, moisture contents, sulfur and ash contents of coal, oil, gas, and wood fuels employed in pulp and paper manufacture are presented in Table 16-2 (3).

Major fuel consumption parameters affecting air pollutant emissions from power boilers in the pulp and paper industry include sulfur and ash contents of the fuels. The SO_2 emissions from fuel combustion are directly proportional to the sulfur content. The sulfur content is normally significant in bituminous coal and residual fuel oil. The major methods for minimizing air pollution from fuel combustion of SO_2 in power boilers are the substitution of low sulfur oil, coal, or natural gas for high sulfur fuels and the construction of tall stacks for dilution of ground level SO_2 concentrations.

TABLE 16-2
CHARACTERISTICS OF FUEL BURNED IN POWER BOILERS AT PULP AND PAPER MILLS IN THE UNITED STATES (3)

	Heating Value (As Fired)			% by Wt. Content of		
				Moisture	Ash	Sulfur
Fuel	Units	Average	(Range)	Average (Range)		
Coal	MJ/kg	31	(24-34)	10 (7-15)	8.1 (3.5-15)	1.9 (0.5-10)
	Btu/lb	13,500	(10,500-14,700)			
Oil	MJ/l	41	(34-43)	0.5 (0-1)	0.1 (0.01-0.2)	1.8 (0.1-3.5)
	Btu/gal	149,000	(122,000-155,000)			
Gas	MJ/m^3	38	(37-40)	0.2 (0-1)	Neg.	Neg.
	Btu/cu ft	1,030	(1,000-1,070)			
Wood	MJ/kg	11	(9.3-13)	25 (10-60)	2.9 (0.1-20)	0.1 (0-0.2)
	Btu/lb	4,600	(4,000-5,500)			

The particulate emissions from fuel combustion generally are proportional to the ash content of the fuel and are significant for coal and wood combustion. The ash material contained in the fuel can be removed from the boiler as fly ash in the exhaust gases or as bottom ash in solid form or as liquid slag, depending on the ash fusion temperature. Normally 80 to 95 percent of the ash material is emitted from the boiler as fly ash. Unburned or partially burned fuel aslo can be emitted from the combustion chamber as particulate matter. Devices normally used for particulate emission control on coal-fired power boilers in the pulp and paper industry are electrostatic precipitators or mechanical collectors; mechanical collectors and liquid scrubbers are most commonly used for wastewood- and bark-fired power boilers.

Recent investigations show that other constituents in fuels may also contribute to air pollution. Martin and Berkau (4) report that the nitrogen content of fuels can contribute to the formation of nitrogen oxides, though the reaction between atmospheric N_2 and O_2 is predominant for flame temperatures above 1,300° C (2,400° F). In addition, trace elements, particularly in bituminous coal and residual fuel oil, may be significant air pollutants, such as the nonmetals chlorine (Cl), fluorine (Fl), and phosphorus (P), and the heavy metals, such as beryllium (Be), mercury (Hg), lead (Pb), cadmium (Cd), zinc (Zn), arsenic (As), and selenium (Se). A summary of air pollutant emission factors from specific fuel combustion processes for industrial power boilers is presented in Table 16-3 (5).

TABLE 16-3
UNCONTROLLED AIR POLLUTANT EMISSION FACTORS FOR FUEL COMBUSTION IN POWER BOILERS FOR THE PULP AND PAPER INDUSTRY (5)

	Particulate Matter		Sulfur Oxides		Nitrogen Oxides		Hydrocarbons		Carbon Monoxide	
Fuel Burned	kg Part / 10^6 kJ	lb Part / 10^6 BTU	kg SO_2 / 10^6 kJ	lb SO_2 / 10^6 BTU	kg NO_2 / 10^6 kJ	lb NO_2 / 10^6 BTU	kg CH_4 / 10^6 kJ	lb CH_4 / 10^6 BTU	kg CO / 10^6 kJ	lb CO / 10^6 BTU
Bituminous Coal										
Pulverized General	0.34 (%A)	0.80 (%A)	0.82 (%S)	1.90 (%S)	0.39	0.900	0.0064	0.015	0.021	0.050
Pulverized Wet Bottom	0.28 (%A)	0.65 (%A)	0.82 (%S)	1.90 (%S)	0.64	1.500	0.0064	0.015	0.021	0.050
Pulverized Dry Bottom	0.37 (%A)	0.85 (%A)	0.82 (%S)	1.90 (%S)	0.39	0.900	0.0064	0.015	0.021	0.050
Pulverized Cyclone	0.04 (%A)	0.10 (%A)	0.82 (%S)	1.90 (%S)	1.17	2.740	0.0064	0.015	0.021	0.050
Spreader Stoker	0.28 (%A)	0.65 (%A)	0.82 (%S)	1.90 (%S)	0.32	0.750	0.0064	0.015	0.021	0.050
Fuel Oil										
Residual-Tangential	0.023	0.053	0.46 (%S)	1.06 (%S)	0.115	0.267	0.0005	0.001	0.0005	0.001
Residual-Horizontal	0.023	0.053	0.46 (%S)	1.06 (%S)	0.230	0.535	0.0005	0.001	0.0005	0.001
Distillate-Tangential	0.015	0.035	0.41 (%S)	0.96 (%S)	0.123	0.285	0.0005	0.001	0.0005	0.001
Distillate-Horizontal	0.015	0.035	0.41 (%S)	0.96 (%S)	0.246	0.570	0.0005	0.001	0.0005	0.001
Natural Gas										
Process Boilers	0.006	0.014	0.00048	0.001	0.160	0.372	0.016	0.038	0.0005	0.001
Gas Turbines	0.006	0.014	0.00048	0.001	0.183	0.425	0.016	0.038	0.0005	0.001
Waste Wood										
No Reinjection	1.50	3.500	0.16	0.375	0.43	1.010	0.11	0.250	0.11	0.250
50% Reinjection	1.79	4.150	0.16	0.375	0.43	0.010	0.11	0.250	0.11	0.250
100% Reinjection	2.32	5.400	0.16	0.375	0.43	0.010	0.11	0.250	0.11	0.250

%A = Percent ash in fuel.
%S = Percent sulfur in fuel.

16.2.2 Furnace Characteristics

Each fuel burned must be fired in a separate type of boiler depending on its physical state and burning characteristics. Natural gas is normally burned for steam generation in package type boilers of varying sizes, where the gas-air mixture can be added in a horizontal configuration along one side. Burning residual fuel oil in power boilers is similar to burning in gas-fired boilers where the oil-air mixture is normally added in either a horizontal or corner tangential firing configuration.

The burning of oil requires a more complex fuel delivery system, normally with pumping, than gas. Residual oil is also usually heated in inlet piping by steam tracing to reduce its viscosity and, therefore, prevent plugging of the fuel lines. Tangential firing of oil or gas can result in substantial reductions in nitrogen oxide concentrations as compared to horizontal firing because of the reduced flame temperatures, greater air-fuel mixing, and resultant lower excess air requirements (6).

Burning solid fuels in power boilers, such as coal or wastewood, requires even more complex design than burning oil in power boilers because of the more complex combustion process and the more complex fuel delivery and ash handling systems. The major types of coal-fired power boiler employed in the pulp and paper industry are the spreader stoker, the chain grate stoker (now in limited use), and several varieties of pulverized firing systems, including dry bottom, wet bottom, and cyclone type units, which can be horizontally, tangentially, or vertically fired. The type and design of boiler used depends on the burning characteristics and chemical composition of the coal; these include the ash content, ash softening temperature, fixed carbon content, volatile carbon content, and heating value. More thorough presentations of design parameters for coal-fired power boilers are available in several references (7, 8, 9, 10).

Wastewood- and bark-fired power boilers can burn the wood alone or can be modified to burn other fuels on an auxiliary basis or in combination. Wastewood and bark are burned in power boilers on chain grates in a radiant Dutch-oven type boiler or in a horizontal air-blown suspended firing configuration in a vertical Stirling boiler. Wood handling systems (including hammermill grinding to a given particle size for suspended firing), bottom and fly ash handling systems, and underfire and overfire air controls must be provided. Major fuel characteristics affecting the design of wastewood-fired power boilers include ash and moisture content, particle size variations, and fixed and volatile carbon content. The amount of particulate matter swept from the combustion chamber is normally greater from the horizontal suspension firing units than from the Dutch-oven type units.

16.2.3 Combustion Variables

The most important variable affecting the combustion process is the fuel-to-air ratio, which can be varied between wide limits even when the other variables remain unchanged.

Variations in the fuel-to-air ratio can be expressed as variations in the amount of excess air or as variations in the oxygen content of the flue gas. The variations influence the combustion temperature, combustion efficiency, ignition speed, flame length, flame radiation, and flue gas composition. Poor combustion efficiency increases particulate emissions, while high combustion temperature, together with an oxygen-rich furnace atmosphere, produces oxides of nitrogen.

Appropriate mixing of fuel and combustion air is essential to achieve fast and complete combustion. The design of firing and furnace has the major influence on the mixing, but mixing also can be controlled to some extent by operational variables such as velocity and direction of fuel, and especially air streams. If mixing is not sufficient, part of the fuel remains unburned and results in particulate emissions. The formation of nitrogen oxides is known to be higher in diffusion flames, where mixing takes place in the flame rather than in premixed flames (11). Nitrogen oxide formation increases with both flame temperature and O_2 level in the combustion zone.

16.3 Boiler Types

The major parameters affecting the design of power boilers to minimize potential air pollutant emissions include:

1. Physical state, chemical composition, and burning characteristics of the fuel,

2. Method of firing fuel and mixing,

3. Combustion chamber volume and configuration, and

4. Other operating parameters, such as fuel firing rates, excess air levels, and air distribution.

The type, size, and collection efficiency requirements for the gas treatment system are determined by the gas flow rate and flow conditions from the boiler, the exit gas pollutant concentrations from the boiler, and specific parameters, such as particle size. Whatever the fuel, the air pollutant emission characteristics from power boilers are very much influenced by design and operating parameters.

16.3.1 Gas-Fired Power Boilers

Natural gas-fired power boilers normally are the simplest in design and operation of any of those used in the pulp and paper industry. They require only piping of the gas to the boiler and mixing it with air to provide adequate heat for steam generation; they require no complex fuel or ash material handling systems. To this extent, the design and operation of these boilers are essentially the same as gas-fired boilers in the electrical utility industry, but the units in the pulp and paper industry are normally smaller and generate steam chiefly for process use instead of for driving turbines. The only potential air pollutants from natural gas-fired power boilers are oxides of nitrogen generated at elevated temperatures during the combustion process.

The two major types of natural gas-fired power boilers used in the pulp and paper industry are horizontal- and tangential-fired units. These units differ only in the method of air-fuel introduction to the combustion chamber. The horizontal-fired units employ firing along one side of the furnace; the tangential units use corner-firing. The nitrogen oxide emissions from horizontal-fired units are normally greater than from tangential-fired units because of their characteristically higher flame temperatures.

The lack of radiating particles in a gas flame requires a large furnace volume to ensure sufficient cooling of the flue gas before entering the other parts of a boiler. A certain amount of particle formation is useful and can be achieved with special burner design or with two-phase firing for boilers designed primarily for burning natural gas. Natural gas can also be burned in pulp and paper industry power boilers that are designed primarily for other fuels and where the gas can be used either for startup or combination firing. Because of the relative simplicity of gas firing in combination boilers, the other fuels dominate the design requirements and the boiler emissions.

The major operating variables for gas-fired power boilers are the amount of excess air added and the distribution of primary and secondary air if off-stoichiometric firing is used. Flue gas recirculation to the furnace can also be added to improve combustion efficiency and to reduce excess air requirements. Operating natural gas-fired power boilers at sufficient excess air allows complete combustion, but more important it also promotes nitrogen oxide formation (12).

The sulfur and ash content of natural gas are negligible, and the respective SO_2 and particulate matter emissions are insignificant. Complete combustion assures that minimal emissions of CO and hydrocarbons will occur. The major air pollutants from natural gas combustion are nitrogen oxides, which can be minimized by off-stoichiometric firing, use of minimal excess air, and flue gas recirculation (13).

16.3.2 Oil-Fired Boilers

Oil-fired power boilers are normally similar in design to natural gas-fired units except that they require more complex fuel handling facilities and longer retention times in the combustion zone. The two major types of liquid petroleum fuels burned are No. 2 distillate fuel oil and No. 6 residual fuel oil. Both types of oils require fuel storage, pumping and injection systems, with steam or electrical tracing of fuel lines needed for residual fuel oil to avoid plugging by the highly viscous liquid. Atomization of the oil injected into the furnace from the firing guns is necessary to provide a spray of fine droplets, assuring complete combustion of the fuel. The major potential air pollutants from fuel oil combustion are nitrogen oxides and sulfur oxides, and, to a somewhat lesser extent, particulate matter.

The two major types of furnace configurations for burning fuel oil in pulp and paper industry power boilers are horizontal front-fired units and tangential corner-fired units. These are similar in design to those employed for natural gas firing except that longer retention times in the combustion zone are normally required to assure complete combustion of the oil. Atomizing and mixing promote combustion, and thereby reduce the formation of unburned carbon particles to the practical minimum.

The furnace volume must be sufficiently large enough to prevent the flame from impinging on the cooled walls: a cooled flame would inhibit the last steps of the combustion reactions and result in the emission of carbon soot particles. The volume of the furnace varies directly with the released thermal energy, and the formation of nitrogen oxides, in turn, is proportional to this energy. Because a smaller combustion chamber causes an increased heat release rate per unit volume, an increase in flame temperature results, which is accompanied by an increase in formation of nitrogen oxides.

Major parameters affecting the operation of oil-fired power boilers are:

1. Excess air level,

2. Air flow distribution pattern,

3. Fuel inlet temperature as it affects oil viscosity, and

4. Amount of steam added for atomization.

The excess air level during fuel oil firing must be carefully controlled within the maximum and minimum limits determined by consideration of both thermal energy conversion efficiency and air pollutant emission levels. The lower practical limit for excess air is reached when carbon particles and combustible gases, such as CO and hydrocarbons, are detected in the flue gas. The upper practical limit for excess air is defined by the formation of significant quantities of nitrogen oxides and the presence of sulfur trioxide (SO_3). Sulfur trioxide formation is accelerated by the presence of trace metal catalysts, such as vanadium (V) in the oil. An additional consideration is that excess air levels above the upper limits result in a decrease in the thermal efficiency of the boiler by increasing the flue gas flow rate and the flue gas outlet temperature.

An important variable in maintaining sufficient atomization is the viscosity of the fuel oil, which is maintained by keeping the oil temperature within rather narrow limits. Increased viscosity at low oil temperatures dampens the vibration of oil droplets and thus reduces the atomization effect. Too high a fuel temperature tends to cause coking of the oil on the hottest parts of the burner and disturbs the atomization process by producing steam and gas bubbles in the oil before it is atomized (14).

The major potential air pollutants from fuel oil combustion are sulfur oxides, nitrogen oxides, and particulate matter.

The SO_2 emissions from fuel oil combustion are essentially a function of the sulfur content of the fuel, which normally ranges from 0.1 to 0.5 percent by weight for light distillate oils and from 0.5 to 3.0 percent, or more, by weight for heavy residual fuel oils, depending on the source of the crude. The major method for controlling SO_2 emissions from oil combustion in the pulp and paper industry, to date, is the substitution of natural gas or low sulfur oil for high sulfur oil. Varying quantities of SO_3, accounting for up to 10 percent of the total sulfur burned, can also be formed during fuel oil combustion. The SO_3 can be hydrolyzed in the presence of water to H_2SO_4 and cause corrosion on cold metal surfaces. The amount of SO_3 formed depends on the sulfur content of the fuel, the excess air level, and the possible presence of trace metal catalysts in the oil; high concentrations of up to 50 or 60 ppm by volume have been observed (15).

Particulate matter emitted from fuel oil combustion consists of inorganic material from the ash content of the fuel and organic materials resulting from incomplete combustion. The organic matter from fuel oil combustion consists primarily of unburned carbon soot particles resulting from incomplete combustion of the oil droplets, approximately 95 percent by weight of the soot particles are less than 10 μm (4×10^{-4} in) in diameter. The carbon content of the particulate matter can be as high as 58 percent by weight, and because of this high carbon content, these particles are not particularly suitable for collection by electrostatic precipitation (16).

The emission of particulate matter from oil firing is strongly dependent on the excess air level during combustion. Any major disturbance in burner operation is almost certain to produce a considerable increase in the particulate matter emissions. The burning of residual fuel oils with sulfur contents above 1.5 percent by weight can cause the particulate matter from the boiler to become saturated with adsorbed H_2SO_4 droplets when the gas stream temperature drops below the acid dew point. The sticky acidic particle deposits can cause rapid corrosion of metal surfaces and, therefore, lower the efficiency of the mechanical cyclone collectors.

Nitrogen oxide controls for oil-fired power boilers are similar to those for gas-fired units; the objectives are to minimize flame temperatures and excess air levels. Nitrogen oxide formation is controlled by off-stoichiometric firing with split air distribution, minimum excess air, and possibly, flue gas recirculation.

16.3.3 Coal-Fired Boilers

Coal-fired power boilers are normally more complex in design than either oil- or gas-fired units because complex solid fuel handling and ash handling systems are required, the fuel injection system is more complicated, and longer retention times with greater air-fuel mixture turbulence levels in the furnace are generally required to assure complete combustion. The main type of coal burned at present for auxiliary power generation in the pulp and paper industry is the bituminous grade from the eastern or midwestern United States. The properties of coals can vary considerably between individual fields. The respective sulfur contents, ash contents, and heating values all affect potential air pollutant emissions. The major potential air pollutants from coal combustion in pulp and paper industry power boilers are sulfur oxides, particulate matter, and nitrogen oxides.

There are several types of coal-fired power boilers employed in the pulp and paper industry. These differ mainly in the methods by which the fuel is added to the furnace, the configurations by which air is added to the combustion chamber, and the boiler bottom configuration. The major coal feed configurations commonly employed in the pulp and paper industry include pulverized firing, spreader stoker, and chain-grate stoker units. The type of unit employed depends on the amount and properties of the coal to be burned. The ash content, ash softening temperature, fixed carbon and volatile carbon contents, moisture content, and, to a lesser extent, sulfur content all influence the type of unit employed. The sizes and shapes of the furnaces are largely influenced by the heating value and ratio of fixed to volatile carbon contents in the coal.

The smaller coal-fired power boilers in the pulp and paper industry are generally either underfeed or overfeed chain-grate stoker units or suspended-firing spreader stoker units. The larger coal-fired power boilers are generally pulverized-firing, employing either vertical, horizontally opposed, tangential corner, or wall-fired units, with either dry or wet bottoms. The pulverized units are employed for coals with high ash softening temperatures, while coals with ash softening temperatures below 1,200° C (2,200° F) are generally burned in cyclone furnaces, though these are not commonly employed in the pulp and paper industry. The design features of the individual types of coal combustion units are extensively reviewed in other references (7, 8, 9, 10).

The particulate emissions in the flue gases from coal-fired power boilers tend to increase with increasing coal ash content and with increasing ash softening temperature. They also basically show the greatest increase where pulverized units employ dry bottoms because of suspension of small particles. Particulate emissions are lowest from pulverized cyclone units because most of the ash is removed as slag from the furnace bottom. The flue gas temperature of the furnace section outlet normally must be maintained below the ash softening temperature of the coal being burned in order to keep particulate matter from melting and sticking on tubes in the superheater section. Coal furnaces must generally be designed to provide sufficient cooling by means of water walls or other methods to prevent superheater slagging. The resultant lower flame zone temperature also acts to reduce nitrogen oxide emissions.

Major air operating variables affecting emissions from coal-fired power boilers include the excess air level and the relative distribution of primary and secondary air (or underfire or overfire air). The excess air level is significant in that increased CO and hydrocarbon emissions are favored by minimum excess air levels. These minimum levels also can increase the carbon content of the particulate matter leaving the boiler. This increased carbon content can adversely affect operation of the electrostatic precipitator by increasing particle resistivity levels. High excess air levels tend to increase the amounts of nitrogen oxides present. Excessive overfire air levels on chain-grate or spreader stoker units can also exert a sweeping action to entrain small particles in the exhaust gases.

Fuel-related operating variables influence particulate emissions from coal-fired power boilers. The fineness of pulverized coal particles is influenced by the degree of grinding, which is a factor that may vary during the lifetime of the grinding elements in the pulverizer. If not controlled, pulverizer wear affects the combustion efficiency by causing progressively larger particles that increase the carbon content in the fly ash. In grate firings, an excessive air flow can penetrate areas in the fuel layer if its deposit on the grate is not of uniform thickness. Localized particulate entrainment results.

The particulate emissions from coal-fired power boilers depend on the ash content of the coal, its ash softening temperature, the method of firing employed, and to a lesser extent on the excess air for organic constituents. Particulate emissions generally are greatest from pulverized dry bottom units, lower from chain grate and spreader stoker units, and lowest from cyclone furnaces. The degree of coal grinding before firing and the type of firing employed both influence the particle size distribution in the exhaust gases. There is insufficient information regarding the particle size distribution from pulp and paper industry coal-fired units at present. It is known, however, that the amount of particulate matter discharged as fly ash relative to the amount of slagged bottom ash increases with ash softening temperature.

SO_2 emissions from coal combustion are directly proportional to the sulfur content of the coal being burned. Increases in excess air level tend to cause increases in SO_3 emissions from coal combustion. But the presence of calcium and magnesium oxides in the particulate matter tends to bind any SO_3 as $CaSO_4$ or $MgSO_4$. Present control methods for sulfur oxides include fuel substitution and the construction of tall stacks. Nitrogen oxide levels from coal combustion tend to increase with combustion zone flame temperatures and excess air levels in the exhaust gases. Nitrogen oxide levels are comparable to those from oil-fired units, except for cyclone furnaces, where the high temperatures required for ash slagging also cause excessive formation of nitrogen oxides.

16.3.4 Wood-Fired Boilers

Waste wood combustion is often employed in pulp and paper mills because the material is readily available from wood debarking or associated lumber and plywood manufacturing operations. The major types of materials that can be burned in waste wood boilers are bark from mechanical or hydraulic debarking operations and waste wood materials, such as sawdust, shavings, slabs, and chips from lumber and plywood manufacture. Major factors affecting waste wood boiler design and use are the quality and amount of material available and its burning characteristics. Waste wood materials are often burned in combination with other fuels such as oil, gas, coal, or clarifier sludge from wastewater treatment. The major potential air pollutant from waste wood combustion is particulate matter; hydrocarbons and nitrogen oxides are also emitted.

The starting point in designing a waste wood firing furnace is different from that for other fuels because bark and wood are waste fuels to be incinerated. The objective of firing waste wood is to maximize the use of the released energy from waste wood to minimize the amount of other fuel to be purchased.

Major design parameters for waste wood boilers are heating value of the fuel, moisture content, ash content, particle size, waste type, and wood species. The moisture content of the fuel is an important parameter; an increasing moisture content value results in a decreasing net heating value due to increased water evaporation and a resultant increase in the flue gas volume. The moisture content of the fuel depends on the type of debarking and the storage time. Mechanical debarking (10 to 30 percent water by weight) results in a lower moisture content than hydraulic debarking (40 to 60 percent water by weight).

The net heating value for most waste woods is about 17 to 21 MJ per kg of dry wood (7,200 to 9,000 BTU/lb), or 8.4 to 13 MJ/kg (3,600 to 5,400 BTU/lb) on an as-fired basis. The heating value for waste woods tends to vary with wood species. The presence of extractive materials, such as terpenes and tall oils, can substantially add to the energy content of the wood.

The particulate emissions from waste wood combustion vary with ash content and particle size of the material being burned. The ash content can vary from below 1 to 20 percent by weight on an as-fired basis. The sizes and shapes of the wood particles being burned can influence the design of grating systems, the type of firing employed, and the relative distributions of underfire and overfire air in the furnace. Furnace fouling is often found in bark firing, especially when bark is fired together with other fuels. In some cases, small amounts of minerals, gathered in the fuel during storing in sea water or on ground, can lower the ash softening temperature so that it is very sticky in the furnace and cannot be easily removed.

Thw major types of combustion units employed for waste wood burning employ pile burning or suspension burning. The successive operations of water evaporation, volatile carbon distillation and oxidation, and fixed carbon oxidation must occur in series. Flat grate Dutch-oven boilers have been extensively used for waste wood combustion in the past. These employ both underfire- and overfire-air jets as applied to a stationary grate and do not normally require extensive pregrinding of the fuel. Thin bed suspension firing is often used for combination firing of wood and other fuels. It allows higher firing rates and is normally employed for large units. A disadvantage is that it normally requires pregrinding of the wood in a hammermill.

Major operating variables affecting the combustion reactions in wood-fired power boilers are the excess air level, the ratio of overfire to underfire air, the combustion temperature, and the pile or suspension bed thickness to regulate fuel burning rate. The overfire air jets should be located and operated to produce a minimum of entrained particulate matter.

The operation of a grate firing should be as even as possible for the best efficiency, so that its combustion air can be correctly regulated. A grate firing in a separate combustion chamber can be operated with substoichiometric air flow, if the furnace temperature must be kept low, or if the furnace atmosphere must be reducing. If neither of these conditions is required, the grate must have the proper excess air to burn combustible gases before they enter the main furnace.

The major potential air pollutant from wood-fired power boilers in the pulp and paper industry is particulate matter, which can result from either inorganic ash in the wood or from incomplete combustion.

The particulate matter from wood-firing is often large in size, 5 to 10 μm (2 to 4×10^{-4} in) or greater. Its specific gravity is usually low so that the use of mechanical cyclone collectors is not always possible. The electrical properties of the fly ash are not very suitable for electrostatic precipitation because of the high carbon content that causes high particle resistivity. The minerals in the wood can cause abrasion in the collecting equipment and ducts resulting in rapid metal wear (3). More complete analysis and classification of the chemical composition and physical size characteristics of particulate matter emitted from wood-fired power boilers is needed than has been reported to date.

Potential gaseous emissions from wood-fired power boilers are oxides of nitrogen, oxides of sulfur, and hydrocarbons resulting from volatilization of the wood. The nitrogen oxide emissions from wood-fired power boilers are generally lower than for fossil fuel firing because of the large combustion volumes per unit amount of fuel burned, the normally high excess air levels of 50 percent or more, and the high fuel moisture content that results in low flame temperatures of 980 to 1,200° C (1,800 to 2,200° F). Emissions of SO_2 from wood-fired power boilers generally are low because the sulfur content of wood is generally less than 0.1 percent by weight. The emissions of terpenes, hydrocarbons, and other volatile organic constituents by distillation and incomplete combustion vary with wood species, furnace temperature, and retention time. The extent of these emissions as potential air pollutants has not been fully described.

16.4 Particulate Emissions

Particulate emissions from power boilers consist of inorganic ash from the fuel and partially burned or unburned fuel from combustion processes. Both of these components vary considerably with the type of fuel and firing. The relative amount of organic material present depends primarily on the excess air level and retention time in the combustion zone. The ash contents of most fuels used in the pulp and paper industry normally are less than 5 percent by weight, with the exception of coal, which normally varies from 5 to 15 percent by weight. The fly ash in coal consists mainly of quartz, aluminum oxides, iron oxides, and alkali oxides (17). Smaller amounts of trace metals and other materials also may be present. The composition of the ash in coal, wood, or oil depends largely on the source of the fuel.

The amount of unburned carbon in the form of soot and grit is very dependent on the quality of oil firing; while fly ash from the firing of coal and wood normally contains only a few percent unburned carbon. This smaller amount again depends on the quality of firing, on excess air addition, on the ratio of primary to secondary air, and especially on the behavior of the fuel on the grate.

Particulate emissions from power boilers normally do not contain large quantities of trace metals or organic hazardous materials (18).

The control of particulate emissions from coal- and wood-fired power boilers is not normally as complex as other processes within the pulp and paper industry. The problems of control are more similar to those found in the power generation field, and the approaches to their solution are the same. Electrostatic precipitation is the most efficient method for particulate control for coal-fired power boilers; cyclone collectors offer a less efficient, but also less expensive, way for either coal- or wood-fired boilers. Liquid scrubbers or fabric filters are effective for particles below 5 μm (2×10^{-4} in) and offer an alternative to electrostatic precipitation, particularly for wood-fired boilers. Typical particulate emissions from power boilers in the pulp and paper industry are presented in Table 16-4 (3), and typical particle size characteristics for coal- and wood-fired power boilers are presented in Table 16-5 (3).

TABLE 16-4
PARTICULATE EMISSION CHARACTERISTICS FROM SELECTED U.S. POWER BOILERS (3)

Number of Boilers	Percent of Fuel Supplied, Btu Basis				Collector Equipment		Particulate Concentration g/m^3 (gr/cu ft)		Collection Efficiency	Emission Rate
	Coal	Oil	Gas	B/W*	Type**	Pressure Drop in. of water	Inlet	Outlet	%	kg/h (lb/hr)
18	100	0	0	0	C	2.5	4.28 (1.87)	0.85 (0.37)	80	129 (284)
2	100	0	0	0	S	–	–	0.57 (0.25)	–	136 (300)
2	100	0	0	0	P	2.2	11.2 (4.89)	0.98 (0.43)	91	180 (397)
16	0	46	0	54	C	2.7	7.9 (3.47)	1.05 (0.46)	87	140 (309)
2	75	0	0	25	C	3.9	–	0.41 (0.18)	–	73 (160)
2	0	0	62	38	C	2.8	5.3 (2.30)	0.39 (0.17)	93	70 (153)
2	73	16	0	11	C	2.5	–	2.75 (1.20)	–	228 (502)
3	0	25	39	36	C	2.8	4.3 (1.88)	0.71 (0.31)	84	202 (445)
2	0	0	0	100	C	0.2	3.2 (1.40)	0.89 (0.39)	72	44 (96)

*B/W = bark and wood waste.

**C = Cyclone.
S = Liquid scrubber.
P = Electrostatic precipitator.

TABLE 16-5

TYPICAL PARTICLE SIZE DISTRIBUTION OF FLY ASH FROM COAL- AND WOOD-FIRED POWER BOILERS (3)

Particle Diameter μm (in)	Percent by Weight of Particles in a Given Size Range					
	Coal-Fired Power Boilers					Bark-Fired Power Boilers
	Pulverized Coal	Cyclone Furnace	Spreader Stoker	Traveling Grate	Underfeed Stoker	
0-10 (0-4 × 10^{-4})	25	72	11	–	7	12
10-20 (4-8 × 10^{-4})	24	15	12	–	8	10
20-30 (8-12 × 10^{-4})	16	6	9	11	6	7
30-40 (12-16 × 10^{-4})	14	2	10	–	9	6
40-75 (16-30 × 10^{-4})	13	–	12	12	8	14
75-150 (30-60 × 10^{-4})	6	5	17	30	19	16
150^+ (60 × 10^{-4}+)	2	–	29	47	43	35
Total	100	100	100	100	100	100

16.4.1 Electrostatic Precipitators

Electrostatic precipitators are used primarily for coal-fired power boilers in the pulp and paper industry. Electrostatic precipitation is suitable for particulate emission control where high collection efficiency is required, but only a small pressure drop can be tolerated. The capital cost of electrostatic precipitators is relatively high, and electric power is consumed during their operation. The particulate collection efficiencies are lower for oil-fired or wood-fired boilers because the carbon content of the fly ash causes considerable increases in particle resistivity as compared to coal-fired units.

The design of electrostatic precipitators depends on gas flow rate, gas temperature, gas humidity, inlet dust loading, and the electrical properties of dust, such as particle resistivity. The resistivity essentially defines the design migration velocity of the particles to the collection electrodes. The gas flow rate determines the design gas velocity, which defines the necessary width of the precipitator for operation. The particle size distribution in the inlet dust has minor influence on the design of the precipitator, unless a major portion of the dust is less than 1 μm (3.9×10^{-5} in) in diameter. At such small particle sizes, the decreasing particle collection efficiency must be compensated for by reduced gas velocity. The precipitator reduces the particle size distribution by selectively removing the larger particles. On the other hand, when a precipitator failure occurs, the resulting particles emitted are selectively both larger and heavier. This operating characteristic should be taken into account when selecting continuous monitoring equipment (19).

The factor which varies the most in the operation of an electrostatic precipitator is the gas velocity or gas flow rate, which varies with boiler load and, in combination boilers, with fuel-to-fuel ratio. Smaller variations in the gas velocity are caused by changes in the gas temperature and in the humidity of the gas. Temperature and humidity are treated as independent variables in determining the efficiency of the precipitator. The humidity of the flue gas depends on the moisture and hydrogen content of the fuel. The quality of the fuel and the firing together cause variations in the unburned carbon content of the dust, which influences the precipitator efficiency and the inlet dust loading. Electrostatic precipitators can be applied to the combination firing of coal and bark.

16.4.2 Cyclone Collectors

Mechanical cyclone collectors are used primarily for particulate emission control on wood-fired power boilers, or as first stage collectors for coal-fired units. In a cyclone collector, the flue gas with its dust burden is fed into a centrifugal field, where centrifugal forces separate dust particles from the flue gas. Single cyclones or multicyclone equipment is used. Multicyclones consist of a group of small cyclones arranged in parallel. The minimum particle size collected by a single cyclone is about 10 μm (4×10^{-4} in); while multiple cyclones will collect 5 μm (2×10^{-4} in) particles. A separated flow with high dust content may further be conducted into a secondary separation with cyclones, and the flue gas recirculated to the main collector.

A cyclone collector has a lower capital cost than an electrostatic precipitator and may also be applicable to coal- and oil-fired power boilers. Because of the energy required to maintain centrifugal movement, the pressure drop across the cyclone is inevitably high. Fouling can be serious, especially in multicyclone equipment, where gas and dust must pass through rather small ducts. Therefore, frequent maintenance of equipment may be required.

The design of a cyclone collector depends on gas flow rate, gas temperature, gas humidity, inlet dust loading, density of particles, and particle size distribution. The abrasive properties of particles may set special requirements for materials used in construction of cyclones and associated ductwork; while the temperature and humidity of gas have their effects on fouling, particularly for bark char or sander dust combustion (20).

The gas flow rate from a power boiler defines the size of a single cyclone or the number of cyclones required in multicyclone equipment, depending on the inlet velocity required for effective separation of particles from the gas stream by centrifugal forces. This velocity, in turn, depends on the density and size distribution of particles in the flue gas stream from the power boilers. The circulating movement can be introduced to the gas either by tangential inlet or by radial vanes with axial inlet. The central outlet tube for clean gas may be located either straight ahead in a horizontal cyclone or at the inlet end of a vertical or inclined cyclone, causing a 180° turn and additional separation. A secondary circuit, with a fan to induce suction, may be connected into the separated dust outlet.

A single- or monocyclone-collector is applicable for rather coarse dust and small flow rates. A small boiler firing woodwaste and bark is a typical application. A multicyclone collector allows for large flow rates by adding to the number of cyclones. The cyclone size can be optimized for required separation and pressure drop.

The separation in a cyclone depends strongly on the centripetal acceleration of the gas and, therefore, on the gas flow rate. This must be kept within acceptable limits to achieve operation between inadequate separation at low velocity and too high a pressure drop at high velocity. Flow rate can be controlled by shutting off certain parts in a multicyclone collector; otherwise, a low collection efficiency must be expected at low boiler loads.

The particle size distribution may change along with boiler load, different fuels, and other changes in firing. Therefore, the collection efficiency of a cyclonic collector also changes. There is no general rule to control the particle size distribution during firing except to try to maintain relatively uniform conditions.

16.4.3 Liquid Scrubbers

Liquid scrubbing is used primarily for particulate collection on wood- and bark-fired power boilers in the pulp and paper industry. Scrubbing traps the particulate matter entrained in the gas stream in liquid for subsequent removal and disposal. Liquid scrubbing has the advantages of being able to remove gaseous and particulate materials simultaneously, of removing fine particles below 1 μm (4×10^{-5} in) in diameter, of recovering additional thermal energy by cooling the gas stream, and possibly of improving primary clarifier sludge settling characteristics. Vertical impingement and venturi scrubbers have been the primary types of unit employed, to date. Successful installations were reported in Montana by Effenberger (21), in Texas by Ritchey (22), and in South Carolina by Pearce (23).

Several major variables affect the design of liquid scrubbing systems for particulate emission control on wood-fired power boilers. Major gas stream variables include the overall gas flow rate, fuel firing rate, flue gas temperature and moisture content, and the allowable scrubber pressure drop as determined by fan capacity characteristics. Major particulate matter characteristics include the total particulate mass concentration and the particle size distribution, particularly for particles less than 10 μm (4×10^{-4} in) in diameter. Liquid-phase design parameters include the makeup and recycle shower rates, liquid pumping capacity, nozzle configurations and sizes, and allowable slurry solids concentrations. The physical configuration and gas-liquid contact geometry chosen are determined by the type of scrubber purchased or designed. The materials of construction, such as stainless steel, must be chosen to avoid corrosion, abrasion, and thermal damage.

The operation of a liquid scrubber is influenced primarily by the liquid phase parameters such as recycle flow rate, makeup water flow rate, nozzle liquid pressure drop, and slurry solids concentration. Gas phase pressure drop is usually subject to a certain amount of adjustment, but is also influenced by the gas flow rate as determined by fuel firing rates. The scrubbing systems described by Effenberger (21) and Ritchey (22) operate at gas pressure drops of about 15 to 25 cm (6 to 10 inches) of water and are able to achieve particulate mass concentrations at standard conditions of 0.02 to 0.05 g/m^3 (0.01 to 0.02 gr/cu ft) or less, corresponding to particulate mass removal efficiencies of 99 percent or greater. Detailed particle size measurements for these units were not provided on either inlets or outlets to the respective collectors. Liquid pH must be controlled to avoid corrosion, particularly if coal or oil is burned in combination with wood. Liquid scrubbers can prove particularly useful to upgrade the particulate collection efficiencies of existing mechanical cyclone collectors on wood-fired power boilers.

16.4.4 Fabric Filters

Fabric filters have not been extensively used for particulate collection on power boilers in the pulp and paper industry. They have the advantages of high removal efficiencies for fine particles of less than 1 μm (4×10^{-5} in) in diameter with pressure drops of 8 to 15 cm (3 to 6 in) of water. There is not enough operating experience with fabric filtration, to date, on wood-, coal-, or oil-fired power boilers in the pulp and paper industry to present detailed design and operating parameters.

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CHAPTER 17

PROCESS MONITORING

17.1 Source Measurements

To determine compliance with existing and proposed pollutant emission standards and to inventory material losses, the types and amounts of gaseous and particulate materials from pulp and paper mill flue gases must be measured. Developing methods for direct and accurate measurement of air pollutant levels for TRS compounds, oxides of sulfur, and particulate matter is important because of increasingly stringent emission standards in all levels of government.

Source testing of particulate matter emissions from pulp and paper mill flue gas streams can be performed by both batch- and continuous-sampling methods. Batch testing provides an average concentration value for a given time period. Continuous monitoring provides a record of instantaneous concentration values over a prolonged time interval to determine compliance with air pollution regulations and to act as a monitor of process equipment operation. Continuous monitoring instruments normally necessitate a higher capital cost than batch sampling equipment, but manpower requirements are normally lower once these systems are placed in operation and maintained by competent, trained personnel.

The successful operation of continuous monitoring systems for measuring particulate matter and gaseous emissions requires instrumentation that is accurate, reliable, stable, reproducible, of simple operation and low maintenance requirements, and subject to minimal interferences. In the design and operation of continuous monitoring instrumentation, both the sample handling and detector systems must be considered. A suitable system for reducing and reporting the voluminous amounts of data that can be generated is also needed.

17.2 Gaseous Monitoring

The major classes of gaseous pollutants emitted from pulp and paper industry sources that may require continuous or batch monitoring are malodorous sulfur compounds, oxides of sulfur, oxides of nitrogen, and organic nonsulfur compounds. The major malodorous sulfur compounds of interest include H_2S, mercaptans, dialkyl sulfides, and dialkyl disulfides. These are commonly classified together as TRS compounds.

The major oxides of sulfur include SO_2 and SO_3 from combustion processes where sulfur-containing fuel is burned. Oxides of nitrogen of interest include NO and NO_2 from combustion processes. Organic nonsulfur compounds include aliphatic, olefinic, and aromatic hydrocarbons, terpenes, phenols, and other organic compounds from kraft and sulfite mill sources.

Gaseous monitoring systems normally have similar, and in some cases, common, sample conditioning systems. The different gaseous constituents are monitored by gas detection devices that depend on the constituent monitored.

17.2.1 Sample Conditioning Systems–General

The purpose of the sample handling and conditioning system is to remove the sample from the flue gas and transfer it to the detector for subsequent analysis without changing the concentration or character of the constituents to be measured. The major elements of the sample conditioning system are the sample probe, the liquid scrubber, the preselective gas separator, the transfer tubing, and the prime mover, as shown in Figure 17-1 (1).

17.2.1.1 Sample Probe

The sample probe is located internally within the stack to remove a portion of the moving gas stream from the duct into the sample conditioning system. A straight stainless steel tube with a 90 degree bend is sufficient for flue gas streams containing negligible quantities of particulate matter, such as digester, washer, evaporator, and black-liquor oxidation tower gases. The probe should be aligned so that any condensate formed drains away from the stack towards the scrubber.

The particulate matter present in flue gases from recovery furnaces, lime kilns, and smelt tanks must be removed by one of two types of filtration systems. The system devised by the National Council for Air and Stream Improvement employs an open end 25 mm (1 in) diameter tube packed with glass wool for particle removal that must be cleaned and repacked periodically to prevent plugging (2).

The system devised by Thoen (3) is designed to prevent plugging by using a porous ceramic probe equipped with a compressed air blowback feature that is actuated by solenoid valving and a timer for 30 second intervals once each 10 minutes. The ceramic probe is normally employed in particulate laden gas streams above their dew points where condensation is not likely, such as in power boilers and kraft recovery furnaces. Where significant quantities of SO_3 are present, such as from oil-fired power boilers, the sample probe should be heated to 150° C (300° F) or higher to prevent condensation of sulfuric acid.

17.2.1.2 Conditioning Device

The major purpose of the conditioning device is to prevent condensation of water vapor in the gas stream. One approach calls for passing the gas stream from the sample probe to the

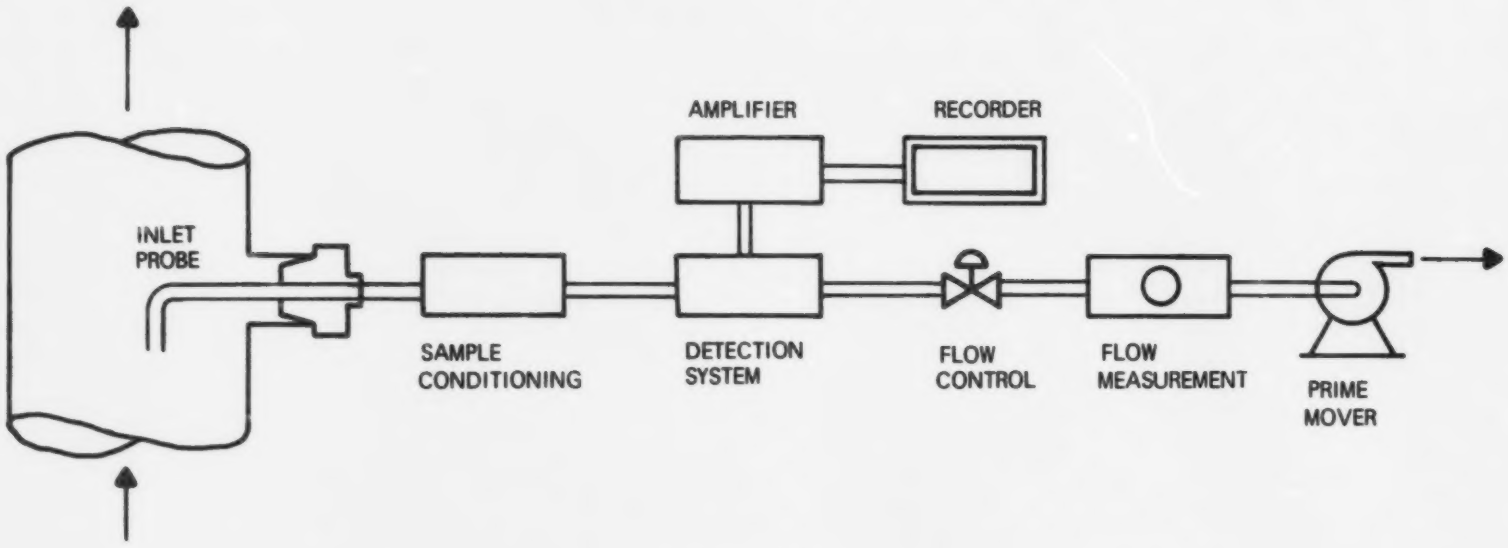

AMPLIFIER
RECORDER
INLET PROBE
SAMPLE CONDITIONING
DETECTION SYSTEM
FLOW CONTROL
FLOW MEASUREMENT
PRIME MOVER

FIGURE 17-1

GAS SAMPLE HANDLING & CONDITIONING SYSTEM FOR EXTERNALLY LOCATED CONTINUOUS GASEOUS MONITORING SYSTEM detector through a line heated to a temperature above its dew point. Maintaining the sample lines at above 110° C (230° F) is normally necessary. Inlet sample probes must also be heated to 150° C (300° F) or higher to effect evaporation, particularly if there are mist droplets entrained in the gas stream, such as sulfuric acid droplets.

A second approach is to employ some type of condenser in the sample line downstream of the probe. The condenser serves the dual functions of removal of the water vapor and cooling of the gas stream before it enters the detector. The condenser can effectively remove the water if the gas stream is cooled to 30° C (86° F) or lower, but it is normally necessary to acidify the condensed moisture to a pH of 2.0 or less by adding H_2SO_4 to minimize absorption of SO_2.

Under some circumstances the gas stream should be diluted with air upstream of the detector to cool the gas stream or to prevent condensation. To control the air flow rate into the system accurately, the exact degree of dilution must be known. This dilution technique is not suitable for extremely low gas concentrations approaching the sensitivity of the detector.

17.2.1.3 Prime Mover

The remaining portions of the gas handling and conditioning system are the flow measurement and control section, the drying section, and the prime mover. A desiccant, such as silica gel or Drierite, can be used to protect either the flow meter or the vacuum pump downstream of the detector, but it is not commonly used. Micrometering needle valves made of stainless steel can be used to control the gas flow rate, since they are able to resist the corrosive gas conditions. Flow metering is done with a rotometer or orifice flow meter.

The prime mover can be located either upstream or downstream of the detection cell depending on the system in use. A positive displacement vacuum pump that is leakproof and sealed may be put in use upstream of the detection unit. Upstream location of the vacuum pump is particularly desirable if a considerably larger volume of stack gas is removed from the duct than is sent to the detector, or if the detector must be operated under positive pressure. Such an arrangement does involve potential problems of particulate plugging and moisture condensation, as well as sample dilution by air leakage. Location of the prime mover downstream of the detection cell allows use of either a mechanical vacuum pump, or a steam, air, or water aspirator.

17.2.1.4 Sampling Lines

Sampling lines should be of sufficient diameter to provide for minimum pressure drop, but small enough for minimum retention time. Tubing of 0.635 cm (0.25 in) to 1.27 cm (0.5 in) is normally optimum for sample line construction. Wall materials of inert polyethylene or Teflon should be used to avoid possible losses by physical adsorption or chemical reaction.

Also, electrically heated Teflon tubing is commercially available for sampling lines of up to 60 m (200 ft) in length. Tygon and rubber tubing, plus carbon steel, cast iron, and copper fittings all react with sulfur compounds and should not be used.

17.2.2 TRS Monitoring Systems

The major malodorous sulfur compounds of interest for continuous monitoring applications in kraft pulp mills include H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3. Major sources of H_2S from the kraft process include the recovery furnace, smelt tank, lime kiln, multiple-effect evaporator, and tall oil vent gases. Major sources of the organic sulfur compounds include the digester blow and relief gases, brown stock washer hood and seal tank vents, multiple-effect evaporator noncondensable gas and condensate liquid streams, black liquor oxidation tower exhausts, and the recovery furnace used following direct contact evaporation. The organic sulfur compounds can often create problems in sample handling because of their tendency to condense and adhere to tubing walls.

17.2.2.1 Gas Conditioning

Accurately transferring TRS compounds from the flue gas to the detector is complicated by the presence of large quantities of water vapor and particulate matter in the flue gas at elevated gas temperatures. Terpenes, SO_2, and organic sulfur compounds can be interfering constituents in coulometric detection systems.

It is first necessary to remove sulfur dioxide from combustion sources such as recovery furnaces, lime kilns, and smelt tanks. A liquid scrubber is located immediately downstream of the probe which contains a solution of potassium acid phthalate ($KHC_8H_4O_4$). The purpose of the scrubber is to selectively remove sulfur dioxide from the flue gas, condense excess water vapor, remove additional particulate matter, and cool the gas stream from stack to ambient temperature conditions. Two different types of potassium acid phthalate scrubbers can be used, the continuous flow and the batch, nonflow types.

The NCASI continuous flow scrubber employs a two chamber system containing liquid absorption and overflow chambers in series. A three percent solution of potassium acid phthalate passes from a storage bottle through a glass wool filter in the bottleneck to remove particulate matter to prevent plugging (2). The liquid flow rate to the scrubber is controlled by a limiting flow orifice of capillary tubing at a rate between 0.5 and 1.0 cm^3/min, which requires replenishment once per week. Gas is drawn at a rate of 25 cm^3/min through the scrubber of 40 cm^3 capacity. A 1.0 m (3 feet) long dropleg is used to maintain suction and prevent leakage.

TRS losses, as H_2S, are between 0.1 and 0.2 ppm by volume at a liquid flow rate of 1.0 cm^3/min because of the finite solubility of the compounds in the $KHC_8H_4O_4$ solution. However, the TRS losses increase considerably with increasing liquid flows above this rate.

The scrubbing system developed by Thoen (3) is a batch system employing a saturated solution of $KHC_8H_4O_4$ which requires replenishment once every 30 days and which has lower total reduced sulfur losses once the system reaches equilibrium. As the solution is depleted, SO_2 removal is less efficient, and may cause interferences in the detector. Condensation at water vapor in the system may also cause malfunctions in the system.

After the SO_2 scrubber, the gas stream passes through a system employing preselective scrubbers where analytical selectivity can be obtained between the respective reduced sulfur gas constituents. Thoen (4) developed scrubbing solutions which could be used for selective removal of H_2S, H_2S plus CH_3SH, and H_2S plus CH_3SH plus CH_3SCH_3. Respective constituent concentrations are monitored by differences in instrument readings. The solutions used are listed in Table 17-1.

TABLE 17-1
SELECTIVE PRESCRUBBING SOLUTIONS FOR SULFUR GAS SEPARATION (4)

Gases Removed	Scrubbing Solution	Concentration % by wt.
SO_2	$KHC_8H_4O_4$	3
$H_2S + SO_2$	$CdSO_4 - H_3BO_3$	1-2
$H_2S + SO_2 + RSH$	NaOH	10
$SO_2 + H_2S + RSH + RSR$	$AgNO_3$	0.5

An additional procedure used on certain gas conditioning systems is to pass the flue gases through a combustion furnace at a temperature of approximately 815° C (1500° F) to convert the reduced sulfur compounds to SO_2 upstream of the detector (5). Conversion of the reduced sulfur compounds to SO_2 makes it feasible to use SO_2 sensitive detection methods, such as flame photometry and ultraviolet spectrophotometry in addition to coulometric titration. An additional advantage of the combustion process is that it converts potentially interfering organic compounds, such as terpenes and olefinic and aromatic hydrocarbons to nonreactive CO_2 and water. The combustion step is necessary for kraft mill sources containing extensive quantities of terpenes, such as digester blow and relief gases, washer hood and seal tank vents, and black-liquor oxidation tower exhausts.

17.2.2.2 Gas Detection Systems

Available detectors for continuous monitoring of reduced sulfur compound levels in kraft pulp mill process streams include coulometric titration, electrochemical membrane sensing, flame photometry, and ultraviolet spectrophotometry. TRS monitoring is complicated by interference from SO_2 and by the sensitivity of some detectors to only H_2S and SO_2. It is often either necessary or desirable to convert the organic sulfur compounds and H_2S to SO_2 by oxidation upstream of the detector, particularly when using detection methods other than coulometric titration.

Coulometric titration is useful for measuring concentrations of H_2S and organic sulfur gases in kraft pulp mill flue gases; but it is also sensitive to olefinic and aromatic hydrocarbons, terpenes, acrolein (CH_2CHCHO), and NO_2 (6).

The technique operates on the principle that the H_2S, SO_2, and organic sulfur compounds present are oxidized to sulfate ion by the action of a halogen electrolyte. A certain electrical current is required to maintain a constant concentration of halogen gas generated from the electrolyte. The current level is proportional to the overall concentration of reactive gases passing through the detection cell (7). Coulometric titration is sensitive to all compounds that can be oxidized by the halogen in varying degrees peculiar to each compound and is not specific to any one compound.

A commercially available instrument employs a solution of 16 percent hydrobromic acid (HBr) as the electrolyte with sensing, generating, and reference electrodes all located on a common shaft (8). The detection cell can be actuated to generate a series of fixed levels of bromine gas (Br_2) by changes in instrument attenuation setting corresponding to concentration ranges varying from 1 to 800 ppm full scale as H_2S.

Flue gas is drawn into the cell where the presence of reactive gases is detected by the consumption of bromine gas generated as the result of the chemical oxidation reactions. The current required for maintaining a constant bromine level in the cell increases as the total concentration of reactive gases increases. The current is converted into an equivalent voltage potential in an amplifier and the signal is transmitted to a continuous printout on a 0 to 100 mv recorder.

Calibration of individual cells for particular gases to be measured is necessary to assure accurate results. The reason is that the response of the instrument to the gases passing through the cell depends both on their concentrations and on the valence states of the sulfur atoms relative to bromine. Each gas then must be calibrated individually to determine its relative response in the cell. The response to particular gases also varies between individual detection cells because of differences in hydraulic characteristics, background noise level, and quality control. A summary of approximate calibration factors for sulfur gases observed for a Barton coulometric titrator is listed in Table 17-2 (9).

TABLE 17-2
APPROXIMATE RANGES IN CALIBRATION FACTORS FOR SULFUR GASES WITH COULOMETRIC TITRATOR (9)

	Concentration Factor (ppm by volume/scale unit)				
Attenuation	H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3	SO_2
0.1	0.008-0.013	0.014-0.016	0.035-0.040	0.030-0.035	0.03-0.04
0.3	0.030-0.035	0.040-0.045	0.090-0.100	0.09-0.12	0.09-0.12
1.0	0.09-0.12	0.12-0.13	0.31-0.37	0.25-0.30	0.30-0.35
3.0	0.24-0.26	0.35-0.38	1.0-1.2	0.5-1.0	0.9-1.0
10.0	0.7-0.9	1.2-1.4	3.5-4.0	2.0-3.0	2.5-3.5
30.0	1.5-2.5	3.0-3.5	11.0-12.0	5.0-8.0	8.0-10.0
100.0	4.5-9.0	10.0-13.0	35.0-40.0	20.0-25.0	25.0-30.0

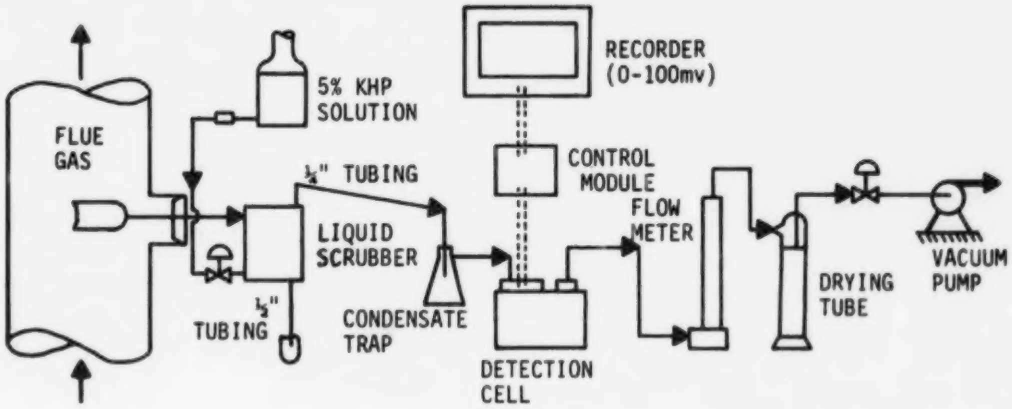
Cells should be calibrated on a weekly basis to assure continued accuracy, particularly for high concentration levels (above 50 ppm by volume as H_2S) because of cell response drift. The electrolyte solution must be changed at least once per month to avoid depletion. The system also appears to require frequent maintenance and suffers from particulate plugging in the cell. Three possible arrangements for the system are illustrated in Figure 17-2.

Electrochemical membrane cells that are specific for either SO_2 or H_2S can be used for monitoring reduced sulfur gas emissions. It is normally necessary to convert the reduced sulfur compounds to SO_2 in an oxidation furnace upstream of the SO_2 selective membrane cell. The H_2S selective membrane cell cannot be used to measure TRS levels in kraft pulp mill flue gases because of interferences from organic sulfur compounds.

The principle of operation is similar to that of coulometric titration. SO_2 operates as the working material in a specially constructed electrochemical transducer cell of proprietary design. The detection cell is a totally enclosed system where the gas sample passes adjacent to a semipermeable plastic membrane across which the SO_2 or H_2S diffuses into the electrolyte solution. The gas produces a change in the electrochemical potential across the cell that is directly proportional to the concentration in the gas stream over a concentration range from 0.01 to 5,000 ppm by volume.

The gas handling system for the electrochemical membrane cell is similar to that of the coulometric titrator as shown in Figure 17-3. The two major differences are that it is necessary to locate a leakproof vacuum pump upstream of the detector because the membrane cells must be operated under positive pressure, and a combustion furnace is needed to oxidize the reduced sulfur compounds to SO_2. Parallel detection cells can be located to record both SO_2 and TRS simultaneously. The gas flow to the detector cell is approximately 500 cm^3/min.

A. NCASI SYSTEM(1):


FLUE GAS
5% KHP SOLUTION
RECORDER (0-100mv)
CONTROL MODULE
¼" TUBING
FLOW METER
LIQUID SCRUBBER
VACUUM PUMP
DRYING TUBE
½" TUBING
CONDENSATE TRAP
DETECTION CELL

B. WEYERHAEUSER SYSTEM(2):

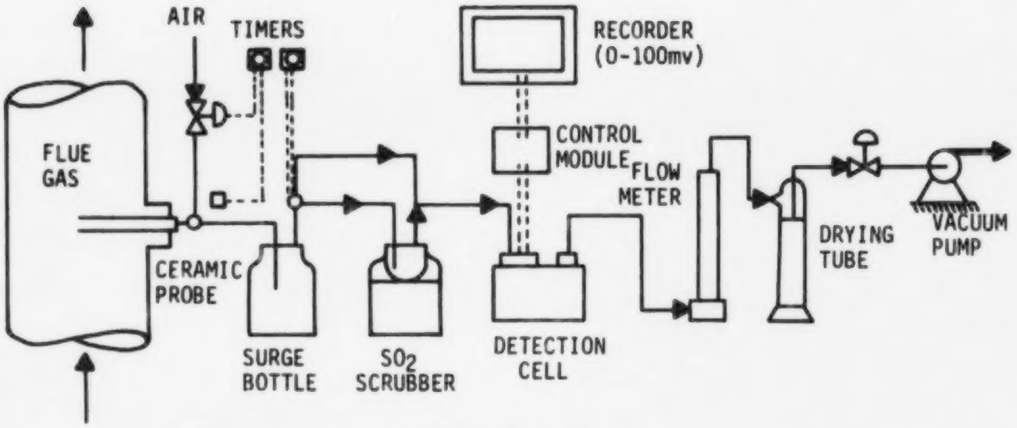

AIR
TIMERS
RECORDER (0-100mv)
FLUE GAS
CONTROL MODULE
FLOW METER
CERAMIC PROBE
DRYING TUBE
VACUUM PUMP
SURGE BOTTLE
SO_2 SCRUBBER
DETECTION CELL

FIGURE 17-2

CONTINUOUS SOURCE MONITORING SYSTEM FOR REDUCED SULFUR EMISSIONS WITH COULOMETRIC TITRATION

C. HUMBOLT COUNTY SYSTEM(4):

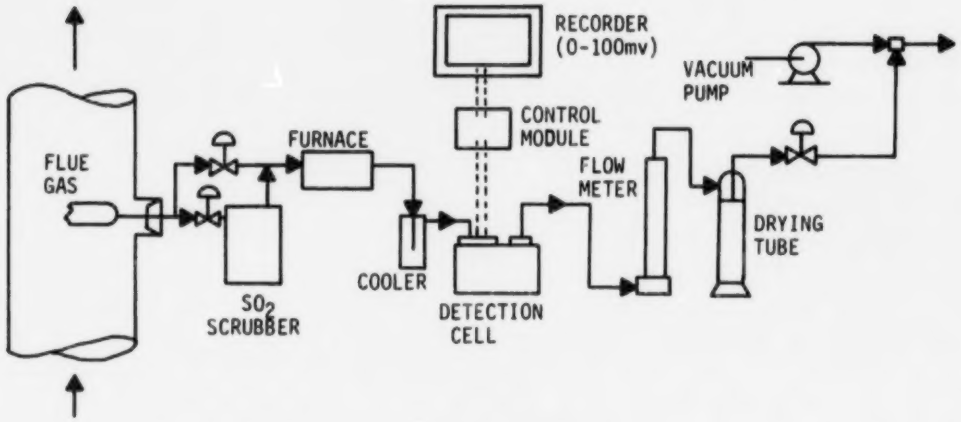

RECORDER
(0-100mv)
VACUUM
PUMP
CONTROL
MODULE
FURNACE
FLOW
METER
FLUE
GAS
DRYING
TUBE
COOLER
SO_2
SCRUBBER
DETECTION
CELL

FIGURE 17-2

CONTINUOUS SOURCE MONITORING SYSTEM FOR REDUCED SULFUR EMISSIONS WITH COULOMETRIC TITRATION–*CONTINUED*

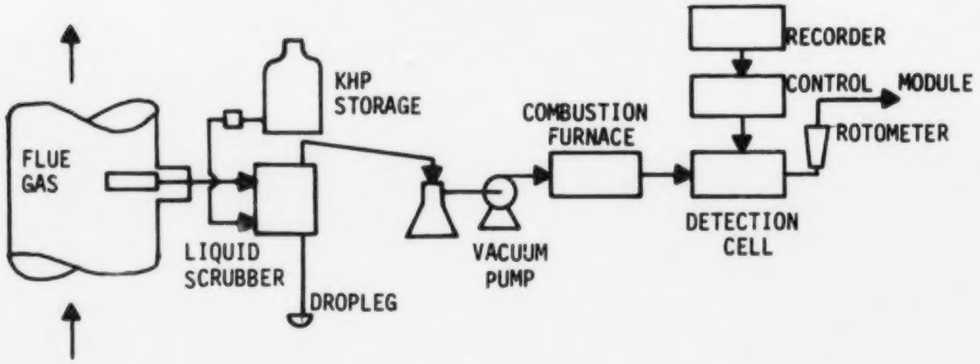

RECORDER
KHP
STORAGE
CONTROL MODULE
COMBUSTION
FURNACE
ROTOMETER
FLUE
GAS
DETECTION
CELL
LIQUID
SCRUBBER
VACUUM
PUMP
DROPLEG

FIGURE 17-3

TOTAL REDUCED SULFUR MONITORING WITH AN ELECTROCHEMICAL MEMBRANE CELL DETECTOR

Spectrophotometric methods are used to measure SO_2 and must be used with an oxidation furnace upstream of the detection device to convert the reduced sulfur compounds to SO_2. Methods of detecting SO_2 are discussed in section 17.2.3.

Some reduced sulfur compounds may be monitored by gas chromatographic methods, as discussed in section 17.2.5.

17.2.3 Sulfur Dioxide Monitoring Systems

SO_2 can be released to the atmosphere from either kraft or sulfite pulp mill process sources or from the combustion of sulfur-containing fuels in coal- or oil-fired power boilers. Major potential sources of SO_2 emissions in the kraft process include the recovery furnace, lime kiln, and smelt tank. The major potential sources of SO_2 in sulfite pulp mills include the digester, evaporator, and acid-making stage vent gases, and the recovery furnace.

A small amount of the SO_2 formed can be subsequently oxidized to SO_3, which is converted to H_2SO_4 mist at temperatures sufficiently below the acid dew point. Normally, the major constituent to be monitored in flue gas streams in SO_2. The SO_2 concentrations can be monitored either within a duct or externally following sample collection and withdrawal.

17.2.3.1 Sample Conditioning

The major constituents making sampling difficult are the large quantities of water vapor and particulate matter in flue gas streams. The SO_2 can be easily removed from the inlet gas stream during condensation of water because of its relatively high solubility. The SO_2 can also react with certain tubing wall materials, resulting in additional loss of SO_2. Therefore, design of the sample handling and conditioning systems must be carefully made to avoid such losses.

17.2.3.2 Detection Systems

Detection systems used for continuous monitoring of SO_2 include electrolytic conductivity, electrochemical transducer conversion, coulometric titration, and ultraviolet spectrometry. The first three are all located externally from the stack and require prior sample withdrawal, while ultraviolet spectrophotometry can be performed either internally or externally. Internal location of the detector eliminates any possible problems caused by air leakage or moisture condensation that might occur during sample withdrawal. External location is the only feasible approach for certain detectors and results in fewer problems with particulate interferences and high gas temperatures.

Miller, Brown, and Abrams (10) describe a continuous monitoring system for measuring total sulfur oxides (SO_2 and SO_3) in the flue gas streams from digester blowpits and acid-making absorption towers in sulfite pulp mills. The stack gas is withdrawn from the duct and passed through a water scrubber. The soluble gases dissolve and pass through an externally located conductivity cell. The relatively simple, inexpensive nonspecific detector is suitable for measurement of sulfur oxide levels in the highly moisture-laden sources because only negligible quantities of interfering, conductivity-producing gases and particulate matter are present in the gas stream.

The gas is withdrawn from the duct at a rate of 3 l/min (0.1 cfm) and mixed with deionized water at a rate of 1 l/min (0.3 gpm). The gas-liquid mixture passes concurrently downward through a 5.1 cm (2 in) diameter tower 66 cm (26 in) long for SO_2 absorption and then into a separation chamber where the gas stream is withdrawn through a vacuum pump. The liquid stream containing the dissolved sulfur oxides is then passed through a conductivity cell that can measure SO_2 concentrations in ranges of either 0 to 1,000 or 0 to 10,000 ppm by volume. A 10 mv recorder is used. The system, as illustrated in Figure 17-4, has proved successful over extended periods of operation.

Electrochemical transducer membrane cells can be employed for selective measurement of SO_2 concentrations in combustion unit and process source flue gases. The principle of operation was discussed in section 17.2.2.2.

Electrochemical membrane cells specific for SO_2 are relatively free from chemical interferences from oxides of nitrogen, SO_3, water vapor, and hydrocarbons. They maintain a relatively stable calibration without substantial drift in response for extended periods with minimum maintenance. The major operating difficulties are that the presence of particulate matter tends to plug the membranes, water vapor condensation in the detector causes erratic response, and the presence of H_2SO_4 mist can cause severe corrosion. The detection cells must be replaced about once per year as the electrolyte solutions become depleted.

A continuous SO_2 monitoring system that uses an electrochemical transducer cell has been described in the literature (11). The sample conditioning system consists of a ceramic heated probe through which gas is withdrawn at a rate of 500 cm^3/min through a heated sample

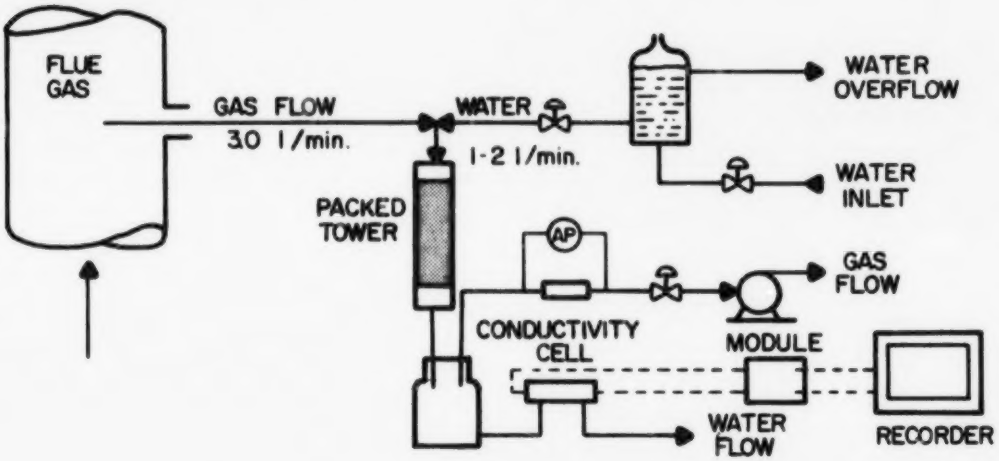


FIGURE 17-4

CONTINUOUS CONDUCTIVITY MONITOR FOR MEASURING SULFUR OXIDE EMISSIONS FROM SULFITE MILL SOURCES (10) line. The gas stream is pulled by a leakproof stainless-steel vacuum pump with a Teflon diaphragm located upstream of the detector because of the necessity of operating the transducer cells under positive pressure. A refrigerator and condenser are used to remove water vapor as it is necessary to maintain a strongly acidic medium to avoid absorportion of SO_2. The gas stream then flows into the detection cell for subsequent analysis, amplification, and recording. The system is illustrated in Figure 17-5.

The system has proved successful during extensive field use but requires replacement of the modular transducer detection cells at intervals ranging from 6 to 18 months, depending on cell design and SO_2 level in the flue gas stream.

Coulometric titration can be used for monitoring SO_2 emissions from coal- and oil-fired power boilers and sulfite pulp mill process sources where reduced sulfur compounds are not present. The technique has been described in section 17.2.2.2. Coulometric titration is nonselective for SO_2 and so organic olefins and other materials can interfere. It is, therefore, necessary to add a combustion furnace upstream of the detector in order to oxidize the olefins from oil-fired boiler flue gases to prevent their interference.

The method also requires removal of water upstream of the detector to avoid flooding the cell.

Ultraviolet spectrophotometry is useful for measurement of SO_2 stack concentrations either internally or externally. The method operates on the principle that the degree of ultraviolet

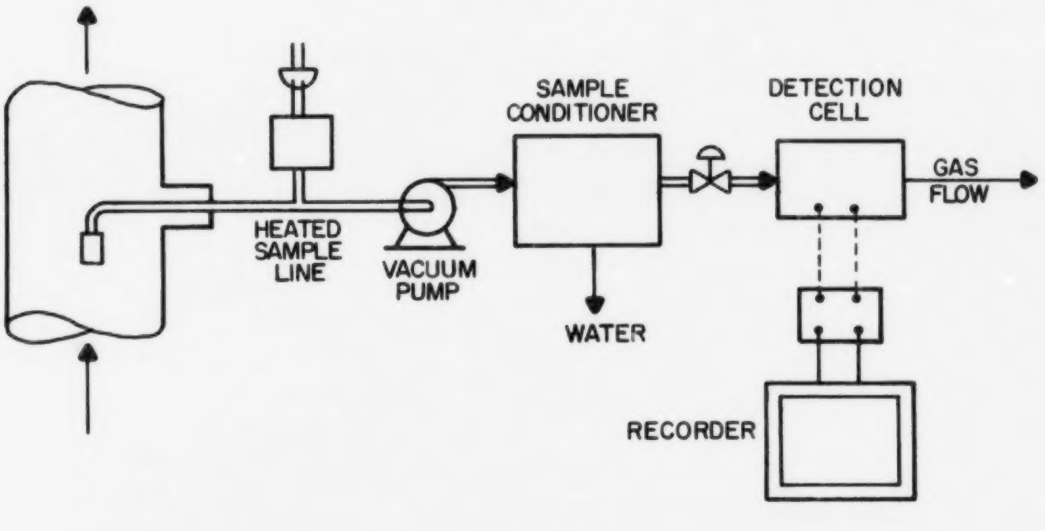


FIGURE 17-5

ELECTROCHEMICAL TRANSDUCER MEMBRANE CELL FOR CONTINUOUS SULFUR DIOXIDE MONITORING (11) radiation absorbed at some characteristic wavelength by passage through a gas stream is proportional to the SO_2 concentration. The method is relatively specific for SO_2 if the proper wavelength ultraviolet light source is used, and it has only minimal interferences from water and particulate matter. Three different modes of ultraviolet spectrophotometry are used in commercially available instrumentation for continuous monitoring of SO_2 levels in flue gas streams.

Thoen, DeHaas, and Baumgartel (12) describe the use of an internally located ultraviolet emission spectrometer for continuous monitoring of SO_2 emissions from a magnesium base sulfite recovery furnace following the absorption towers. The instrument employs a detection system where the ultraviolet radiation from a single beam mercury vapor lamp at a wavelength of 254 nm is passed across a duct through a cylindrical perforated fiber glass tube 2 m (6 ft) long. Gas molecule interchange into and out of the fiber glass tube is facilitated by a series of holes located at 90 degrees to the direction of flow; this orientation inhibits large particles and water droplets from entering. The system is illustrated in Figure 17-6.

The system is suitable for measuring SO_2 concentrations from 80 to 4,000 ppm by volume with an electronic output of 0 to 10 volts DC. The system has a minimum of interferences, is resistant to corrosion, and employs no moving parts. The device is relatively insensitive to low SO_2 concentrations, displays sluggish response to rapid changes in concentration, and the fiber glass is not suitable for high gas temperatures. The mercury vapor lamp at 254 nm wavelength does not correspond to the SO_2 maximum absorbance at 280 nm.

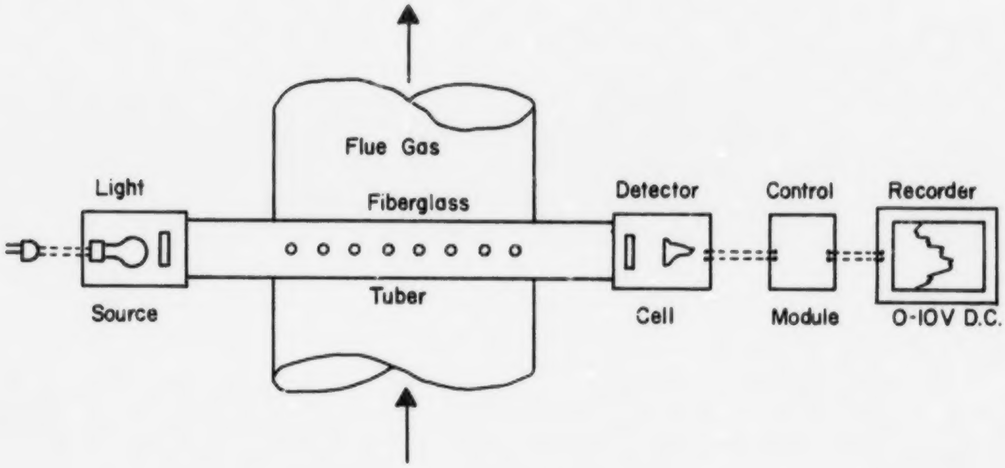


FIGURE 17-6

INTERNALLY LOCATED ULTRAVIOLET SPECTROMETER FOR SULFUR DIOXIDE MONITORING IN FLUE GAS STREAMS (12)

Saltzman (13) describes the use of an externally located dual beam ultraviolet spectrophotometric analyzer for continuous monitoring of SO_2 levels in flue gas streams from coal- and oil-fired power boilers and sulfite recovery furnaces. The gas stream is withdrawn from the duct through a heated porous ceramic probe of 20 μ (7.9×10^{-4} in) porosity to remove particulate matter, as shown in Figure 17-7. The gas sample passes through a heated, electrically traced Teflon tube to prevent condensation of water vapor. The gas stream then passes through the photometric detection cell at a rate of 1 l/min and is drawn through an air aspirator maintained at a constant vacuum. A compressed air purge located upstream of the detection cell is used to remove particulate matter from the probe.

The detection system is a dual beam photometer in which ultraviolet light of 280 nm is passed through the sample cell to provide for specific SO_2 absorbance. Visible light, with a wavelength of 578 nm, is passed through the reference cell so that it is possible to minimize the potential interference from NO_2. The system is heated to prevent water condensation, is rugged and durable under field conditions, and can maintain calibration on a stable basis for extended periods. To prevent small particles from depositing on the detector cell surfaces, a glass wool filter is used in the sample line to remove them (14).

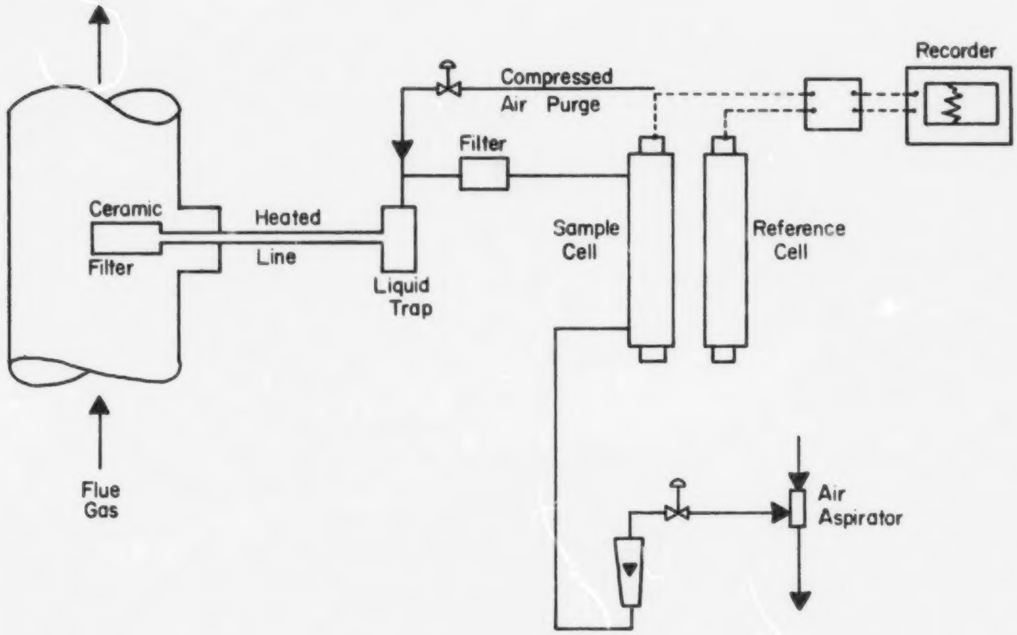


FIGURE 17-7

INTERNALLY LOCATED ULTRAVIOLET SPECTROPHOTOMETER FOR SULFUR DIOXIDE MONITORING IN FLUE GAS STREAMS (11)

An ultraviolet correlation spectrometer, located internally, is used for measuring SO_2 in flue gas streams (15). The system employs a cylindrical slotted probe placed in the gas stream perpendicular to the direction of flow. Ultraviolet light at a series of wavelengths corresponding to the absorbance characteristics of SO_2 are passed from the light source into the stack and reflected from a mirror back into the detector. The degree of absorption of light is proportional to the SO_2 concentration in the flue gas and is indicated in ranges from 0 to 1,000 or 0 to 5,000 ppm by volume.

17.2.4 Nitrogen Oxide Monitoring Systems

Oxides of nitrogen are released to the atmosphere from any combustion process because of the reaction between O_2 and N_2 at elevated temperatures. Approximately 90 percent of the oxides of nitrogen formed is NO with the remainder being mostly NO_2. The potential sources of emissions of nitrogen oxides to the atmosphere are coal-, wood-, oil-, and gas-fired power boilers, recovery furnaces and lime kilns in kraft pulp mills, and recovery furnaces and sulfur burners in sulfite pulp mills.

The possible constituents to be monitored in flue gas streams include NO, NO_2, and total oxides of nitrogen. Continuous monitoring of oxides of nitrogen may be performed either internally within the stack or externally from outside the stack by sample withdrawal. Oxides of nitrogen emissions from kraft and sulfite pulp mill process sources are not normally as significant as from power boilers because large quantities of water present in the spent cooling liquors and lime mud inhibit the occurrence of high flame temperatures.

17.2.4.1 Sample Conditioning

The gas NO is relatively insoluble in water, but NO_2 can be removed during condensation of water unless strongly acidic conditions are maintained. For certain types of detectors, a heated, electrically-traced inert Teflon sampling line can be used if condensation is to be prevented and the detector kept heated. Prime movers employed can be either corrosion-resistant and leakproof vacuum pumps or air, steam or water aspirators. The features for sample handling and conditioning systems for oxides of nitrogen measurements are similar to those employed for SO_2 systems, as described in the previous section.

17.2.4.2 Detection Systems

The major detection systems employed for continuous oxides of nitrogen measurements include electrochemical transducer membrane cells, ultraviolet spectrophotometry, infrared spectrophotometry, and chemiluminescence. Most detection systems employed for continuous oxides of nitrogen measurements are located external to the stack and, therefore, require sample conditioning systems.

Electrochemical transducer membrane cell detectors are available for measuring either NO_2 or total oxides of nitrogen (NO plus NO_2) levels in flue gas streams. The sample conditioning system requires withdrawal of the stack gas sample through a ceramic probe for particulate removal, and a heated line to prevent moisture condensation. The gas is drawn by a sealed, leakproof stainless steel vacuum pump via the sample conditioning condenser into the electrochemical membrane detector. The concentration of NO_2 and/or NO is taken as being proportional to the change in electrochemical potential across the cell with a readout of 0 to 10 mv. Readable concentration ranges are zero to 500, 1,000, or 5,000 ppm by volume.

Ultraviolet spectrophotometry is useful for measurement of oxides of nitrogen levels in flue gas streams. The detection principle is the same as for the SO_2 system described (section 17.2.2.2) except that the wavelengths for the light beams to the sample and reference cells are 436 and 578 nm, respectively, where NO_2 is the chemical compound being measured. A reactor also converts NO to NO_2 at elevated temperature and pressure. The concentrations of NO_2 alone and NO_2 plus NO are read sequentially in a timed cycle.

Infrared spectrophotometry can also be used for measuring of oxides of nitrogen. The principle is the same as for ultraviolet spectrophotometry except that characteristic infrared absorption peaks for NO and NO_2 are used. There is only limited field experience with the technique, to date.

Chemiluminescence is another technique for measuring oxides of nitrogen. Stack gas is withdrawn from the duct, conditioned to remove particulate matter and water vapor, and then passed to a catalytic chemical reactor to form NO_2 and O_2. Light is produced by this reaction, and the intensity of the light is proportional to the inlet concentration of NO. The NO concentration alone is determined by letting the sample (containing both NO and NO_2) bypass the reduction chamber so that NO_2 is not reduced and, therefore, not detected.

17.2.5 Gas Chromatography

Gas chromatography separates constituents of a gaseous mixture by exploiting their differences in relative affinity for a given packing material in a concurrent flow column. These differences cause the various constituents of the mixture to pass through the column at different rates. The gaseous components can then be individually analyzed as they pass the column exit by means of a suitable detector. Gas chromatography provides a versatile means of analyzing for a wide variety of compounds over a wide range of concentrations, but only for discrete samples and not on a continuous basis.

The major elements of a gas chromatograph are the sample collection and handling system, the sample injection system, the carrier gas flow system, the separation column, and the detector. The primary variables in gas chromatography are the sample handling procedure, the sample size, the column dimensions, and packing, the column temperature, and the detector. Compounds of primary interest for measurement by gas chromatography are H_2S and the organic sulfur compounds, plus other organic compounds such as hydrocarbons, terpenes, and alcohols.

17.2.5.1 Sample Handling

The major difficulties in sample handling and conditioning systems are posed by the presence of excessive quantities of particulate matter, water vapor, organic and aqueous mists and droplets, and pulp fibers (15). A cyclone separator that uses an enlarged sample probe with a splatter plate pointed downward in the gas stream is necessary to prevent droplet entrainment in mist-laden gas streams. Porous ceramic or sintered stainless probes or open tubes packed with glass wool can be used to remove particulate matter upstream of the sampling lines for gas streams at temperatures above their dew points.

Water vapor is present in flue gas streams from most pulp mill sources in quantities ranging from 20 to 95 percent by volume. The major methods for alleviating possible losses of gaseous components to be analyzed are to heat the sample probe, sampling lines, and any collection vessels by electric tracing to temperatures above the gas dew points, or to dilute the source gas with dry gas of known composition to below the level at which water will condense at the given temperature.

A possibility that must be anticipated and allowed for in the design and construction of gas sample handling systems is chemical or physical reaction between the gases to be analyzed and the wall materials of the sample lines or containers. Teflon and glass are the most nearly inert wall materials readily available for sampling lines, while 316 stainless valves and fittings are sufficiently inert and corrosion-resistant for normal use. Polyethylene and polypropylene can also be used, but are subject to melting at gas temperatures above 120° C (250° F).

The two major types of sample handling systems are the batch and continuous types. Batch systems in use include the use of cylindrical gas collection flasks and evacuated glass bottles that normally must be heated to 150° C (300° F) or higher to prevent moisture condensation. Sample injection into the chromatograph normally is made by glass syringes of varying sizes. It is sometimes necessary to concentrate samples by freezeout, solid adsorption, or liquid adsorption to have sufficient material to perform analyses.

Continuous sampling systems use withdrawal of the gas sample through a heated line from the source at a relatively high flow rate. Gas samples can be injected into the chromatograph at frequent intervals through a sample loop and port assembly. Dilution of a given sample prior to injection into the chromatograph is sometimes necessary when using detectors, such as the flame photometric unit. Also, to minimize the retention time in the sampling lines, withdrawal of a considerably larger volume of gas than that passed through the sample is, at times, recommended.

17.2.5.2 Column Technology

Selecting the proper column and packing is important to successful analysis by gas chromatography. Pertinent variables in column technology are the column length and diameter, the solid support, the liquid used, and the tubing material. Selection of the proper column is necessary to facilitate the separation of the gaseous components of interest; different gases have different relative affinities for different packing materials.

Gas chromatographic column materials sufficiently inert and temperature resistant for sulfur gas analyses include 316 stainless, glass, and Teflon (16). The sample injection system, the separation column, and the detector must be heated to facilitate many of the sulfur gas separations. Pressure and temperature limits, inertness, and durability must be considered in selecting tubular column materials. The degree of separation between components that can be achieved by a column increases with increasing length and decreasing diameter. Column diameters normally vary from 0.3 cm (0.125 in) to 0.6 cm (0.250 in) with lengths ranging from 3 to 30 m (10 to 100 feet). Carrier gas flow rates will vary from 30 to 150 cm^3/min (15). Teflon column temperatures should not exceed 100 to 150° C (212 to 300° F).

Solid phase support materials must be of sufficient inertness, porosity, uniformity, strength, and ease of packing for generalized use. The separation efficiency of the solid support is directly proportional to its porosity and surface area, but inversely proportional to its inertness. Noninert columns result in tailing of peaks. Normal column solid supports include Chromosorb G, P, T, and W.

The liquid phase of the column separates the various components by either vapor pressure or polarity; in either case molecules of greater molecular weight tend to remain in the column for longer periods. Liquid phase materials in common use for sulfur gas separation include the Carbowax 20X and 1540, polypropylene, glycol, binonylphthalate and polyphenyl ether and Poropak Q (15).

17.2.5.3 Chromatographic Detectors

The major chromatographic detection systems in use for sulfur gas analyses are thermal conductivity, flame ionization, flame photometry, and microcoulometry. The detectors used must have accuracy, stability, sensitivity, selectivity, durability, rapid response, minimum maintenance, and freedom from interfering substances. Thermal conductivity detectors are not specific or sensitive enough for most mill applications, and microcoulometric detectors are unsuitable because they can be easily overloaded at high concentrations and require frequent maintenance.

A summary of detector characteristics is presented in Table 17-3.

The two major detectors in use in pulp mills include the flame ionization and flame photometric units. Both systems are free from water interference, have excellent stability characteristics, and both require hydrogen flames and a nitrogen carrier gas. The flame ionization detector is suitable for organic sulfur and nonsulfur compounds, which can be ionized in flames, but is not sensitive to the inorganic H_2S or SO_2. The flame photometric detector is suitable for H_2S and SO_2, as well as organic sulfur compounds, over the range from 5 ppb to 5 ppm by volume (17). Samples of higher concentrations require either dilution or the use of very small sample loops of 0.5 cm^3 or lower capacity.

17.2.6 Calibration Procedures

Periodic calibration of gaseous monitoring instruments is necessary to their continued accuracy. The typical calibration procedure checks the instrument by using it to measure a gas stream of known concentration. The difference between the known and the measured values is the error of the instrument. Methods in use for preparing known gas concentrations include rotating syringes, motor-driven syringes, flexible fabric bags, known cylinder mixtures, and permeation tubes. Of these, all except the motor-driven syringes are in common use.

17.2.6.1 Rotating Syringe

Rotating syringes can be used for calibration of gaseous monitoring instruments over both ambient and source ranges of concentration. The technique employs dilution of pure gas from a small syringe with air in a large syringe. The large syringe is placed in an upright position and caused to rotate by the action of an airstream directed against its vanes. The flow rate of gas mixture from the syringe is controlled by a calibrated limiting flow capillary, which is usually a broken thermometer. The capillary is inserted into the air stream to form the required gas concentration, which is then fed to the instrument, as shown in Figure 17-8 (18).

The small syringes can range in size from 0.5 to 10.0 cm^3 while the large syringes can be 50 to 100 cm^3. Adding pure gas to the large syringe at extremely high inlet concentrations is sometimes necessary. The thermometer capillaries are individually calibrated by a soap bubble flow meter; the flow rate remains constant because of the constant pressure exerted by the rotating plunger. Flow rates for the capillaries normally range from 0.5 to 5.0 cm^3/min. Air flow rates for the dilution system can vary from 0.5 to 50 l/min (0.018 to 1.8 cfm).

TABLE 17-3
OPERATING CHARACTERISTICS OF GAS CHROMATOGRAPHIC DETECTORS (15)

Detector	Sensitivity ppm, by vol	Stability	Gases Analyzed H_2S	Gases Analyzed SO_2	Gases Analyzed Organ. Sulfur	Gases Analyzed Organ. Comp.	Water Interference
Thermal Conductivity	10	Good	Yes	Yes	Yes	Yes	Yes
Flame Ionization	0.5	Excellent	No	No	Yes	Yes	No
Flame Photometric	0.005	Excellent	Yes	Yes	Yes	No	No
Bromine Coulometric	0.5	Poor	Yes	Yes	Yes	Yes*	No

*For oxidizable organic compounds only.

The rotating syringe method provides a versatile and inexpensive means of providing gas concentrations over a wide range with a minimum of equipment. But the method is not without disadvantages. It does require prior calibration of the capillary flow rate. The syringes are subject to sticking in humid atmospheres. Careful loading is necessary to avoid errors. And it is necessary to rotate the syringe plunger by directing an air stream against its attached vertical rotor; otherwise there is no assurance that a constant delivery pressure is maintained, which is necessary to assure a constant gas flow rate through the syringe capillary.

Permeation tubes provide a versatile and accurate means of calibrating gaseous monitoring instruments. The technique operates on the principle of a constant rate of diffusion of a pure gas through a porous membrane of fixed cross-sectional area and thickness at a given temperature (19). The permeation tube is placed in a chamber immersed in a constant temperature bath, and dilution air is caused to pass through the system. The gas stream containing the dilution air plus the pollutant gas at a specified concentration is then caused to flow from the dilution chamber to the instrument for calibration purposes, as shown in Figure 17-9.

Permeation tubes are made of cylindrical lengths of Teflon plastic filled with liquefied pollutant gas to be measured. They can be fabricated or purchased commercially (20). The constant temperature bath is normally kept at 25 to 27° C (77 to 80° F). The physical

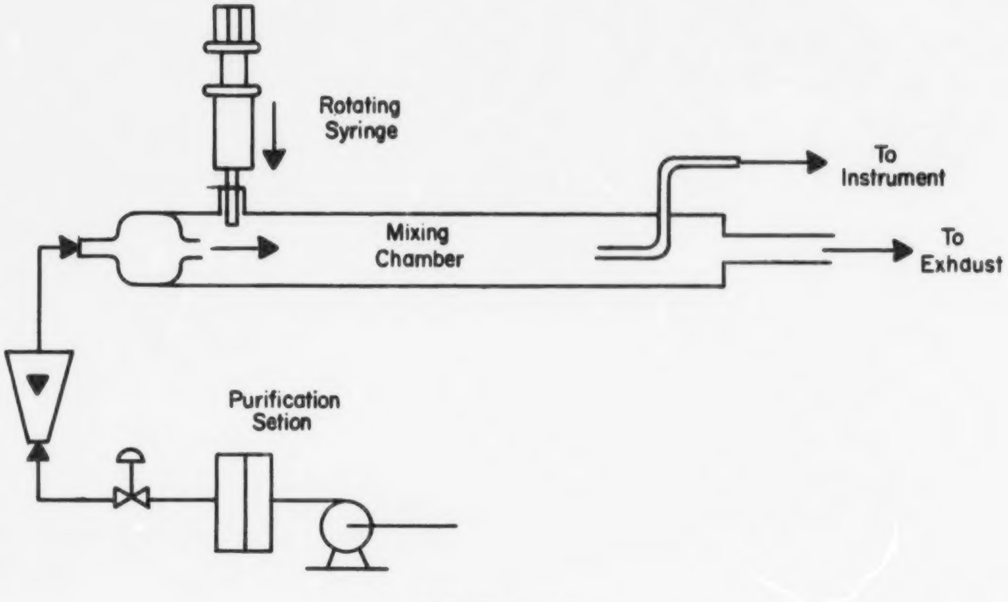


FIGURE 17-8

ROTATING SYRINGE INSTRUMENT CALIBRATION PROCEDURE

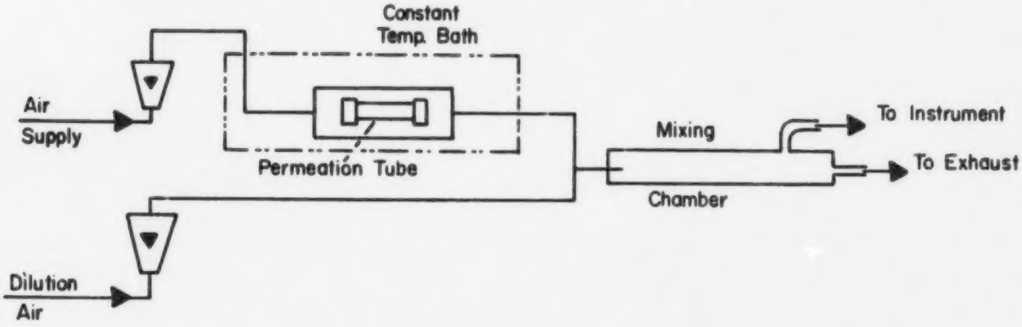


FIGURE 17-9
PERMEATION TUBE INSTRUMENT CALIBRATION PROCEDURE

variables for the permeation tube are its diameter, wall thickness, and length. The primary operating variables are the temperature and the air flow rate. Permeation rates for tubes are normally calibrated gravimetrically in terms of weight loss per unit time.

Permeation tubes require the use of a constant temperature bath and are more cumbersome for field use and more expensive than rotating syringe systems. Newly developed systems now available commercially eliminate the use of liquid baths, resulting in a lighter weight, more compact and less complex unit.

17.2.6.3 Gas Cylinders

Stainless gas cylinders used for calibration of gaseous monitoring instruments are cylinders of given volume. Known amounts of gas are inserted in them and pressurized with either air or nitrogen to produce known concentrations (21). The gas mixture can then be added at a given flow rate to a stream of flowing air to produce a given concentration. The technique is suitable for field use and is simple and inexpensive; however, severe losses can occur during storage for certain gases by adsorption on or reaction with wall materials.

17.2.6.4 Calculation Procedures

1. Rotating Syringe

$$C_I = \frac{C_L\ Q_L}{Q_I} = \frac{V_S\ Q_L}{V_L\ Q_I} \times 10^6$$

where: C_I = concentration fed to instrument, ppm by volume
C_L = concentration in large syringe, ppm by volume
Q_I = flow rate of dilution air, cm^3/min

Q_L = flow rate from large syringe, cm^3/min
V_L = volume of large syringe, cm^3
V_S = volume of small syringe, cm^3

Note.–Because Q_I, Q_L, V_L and V_S appear only in ratios, any consistent units of volume and volume/time may be used.

2. Permeation Tube (20)

$$C_I = 0.0623 \frac{(R)\,(T)}{(MW)\,(Q_I)\,(P)}$$

where: C_I = concentration fed to instrument, ppm by volume
MW = molecular weight of gas, g/mole
P = pressure of calibration system, mm Hg
Q_I = dilution air flow rate, l/min
R = permeation rate, ng/min
T = water bath temperature, °K

17.3 Particulate Monitoring

Particulate sampling and analysis are necessary for recovery furnaces, smelt tanks, and lime kilns in kraft pulp mills, for recovery furnaces in sulfite pulp mills, and for all coal-, wood-, and oil-fired power boilers. Determination of particulate mass concentration is necessary to meet current air pollution regulations, with increasing emphasis being placed on particle size distribution. Batch techniques are specified for determining particulate mass concentrations, emission rates, and size distributions. Continuous monitoring of particulate emissions is gaining increasing emphasis as more accurate and reliable methods are developed (22).

17.3.1 Preliminary Considerations

Particulate matter is normally defined as any material emitted into the atmosphere in either a solid or liquid state, including dusts, fumes, smoke, flyash, soot, tars, droplets, and mists. Changes in physical state with temperature can cause confusion in defining particulate matter for materials such as organic vapors and acid mists. Changes in chemical form, such as oxidation of SO_2 to H_2SO_4 in sampling train impingers after collection, can cause especially serious difficulty in interpreting emission standards.

Particulate matter must be defined as such for either stack or standard conditions. The present definition accepted by the U.S. Environmental Protection Agency is that particulate matter is material collected on a filter of porosity 0.45 μm (1.8×10^{-5} in) which has been heated to 121° C (250° F). Other definitions for particulate matter specified by local agencies include, among others, material collected in liquid impingers at standard conditions.

Particles in pulp and paper mill sources can vary from less than 0.01 to greater than 100 μm (4×10^{-7} to 4×10^{-3} in) in diameter, depending on the source and type of collector used. Sampling at isokinetic conditions is normally necessary because of the inertial properties of particles greater than 5 μm (2×10^{-4} in) in diameter. The normal procedure employed for maintaining isokinetic conditions within plus or minus 10 percent of the actual stack velocity is to locate a pitot tube parallel to the sample probe to measure the gas velocity continuously and to make periodic corrections as needed.

17.3.2 Batch Particulate Sampling

Batch particulate sampling is used to determine total particulate concentrations and emission rates from flue gas streams and is necessary for calibration of continuous particulate monitoring devices. Batch sampling provides an average value for particulate concentration in a duct over a given time period, but does not provide real-time instantaneous values. Collection methods for batch particulate sampling include filtration and liquid impingement.

A low volume system (0.8 to 2.5 m^3/h or 0.5 to 1.5 cfm), specified by the American Society of Mechanical Engineers (ASME), relies on an internally located alundum thimble for particulate collection, as shown in Figure 17-10 (23). The amount of material collected is then analyzed gravimetrically. The standard specifies collection of particulate materials larger than 1 μm (4×10^{-5} in) in diameter. The method is relatively simple and inexpensive, but has several shortcomings. The thimbles tend to pass small particles, particularly during the initial collection period, in direct proportion to increasing thimble porosity. The thimbles are subject to leakage by improper sealing around their gaskets, to plugging and washthrough in wet gas streams, and to dust losses during handling following collection.

The Los Angeles County Air Pollution Control District employs a multiple-stage collection train for particulate sampling in an arrangement similar to that employed by the National Council for Air and Stream Improvement (24). One sampling train employs an internally located heated cyclone and alundum thimble as the primary collection stage, followed by a series of liquid impingers, and a five grade thimble for removal of particles of diameter greater than 0.3 μm (1.2×10^{-6} in).

The vacuum pump is placed downstream of the meter to preclude air dilution of the gas stream. A sampling rate of 0.8 to 1.5 m^3/h (0.5 to 0.9 cfm) is employed. Total particulate matter is then determined by gravimetric analysis of the material collected. The method requires several analyses, and the possibility of sulfate formation from oxidation of SO_2 in the impinger liquid following collection introduces further uncertainty.

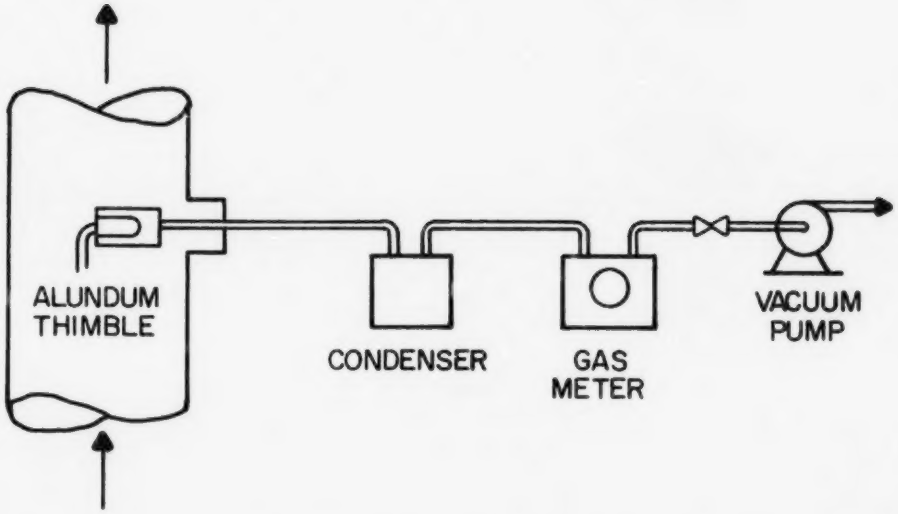


FIGURE 17-10

ASME BATCH PARTICULATE SAMPLING TRAIN

The particulate sampling train, specified by the U.S. Environmental Protection Agency, employs an externally located two-stage collection system as shown in Figure 17-11 (25). The primary collection stage consists of a glass cyclone and a 5 cm (2 in) diameter glass fiber filter of 0.30 to 0.45 μm (1.26 to 1.8×10^{-6} in) porosity that is heated to 121° C (250° F) to avoid condensation. The secondary collection stage consists of a series of Greenburg-Smith liquid impingers containing water. The impingers are used to condense water vapor present so as to prevent flooding the pump and meter and for absorption of potentially corrosive gases. In addition, the water vapor content of the stack gases is determined from the condensate collected in the impinger. The vacuum pump follows the

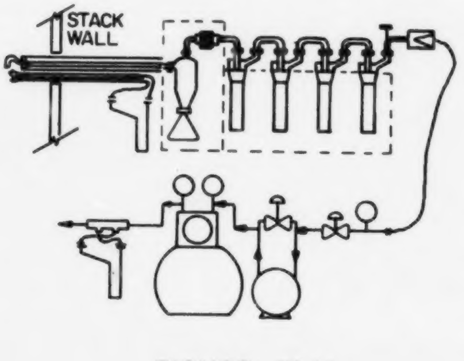


FIGURE 17-11

EPA BATCH PARTICULATE SAMPLING TRAIN

impingers and is followed by the gas meter to measure the volume sampled. An S-type pitot tube, located in parallel to the sample probe, facilitates the maintenance of isokinetic sampling conditions. The system provides for efficient particulate collection, but is cumbersome to handle. The small filters are subject to rapid plugging at high loadings, and large pressure drops tend to develop after prolonged sampling periods.

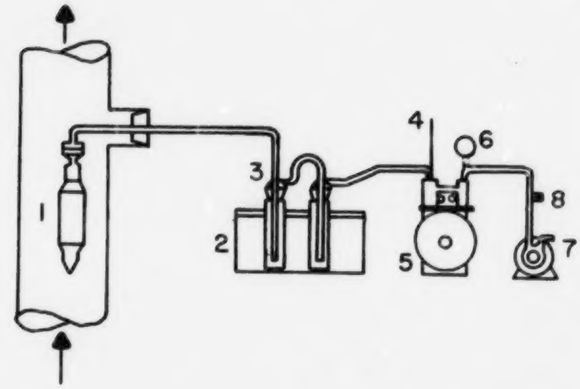
17.3.3 Particle Size Distribution

A major problem in particulate sampling is the determination of particle size distribution in flue gas streams. Particles can range in diameter from less than 0.01 to greater than 100 μm (4×10^{-7} to 4×10^{-3} in), with densities ranging approximately from 0.8 to 2.5 g/cm^3. The problem of determining particle size in gas streams is made especially difficult by the high humidity of the gas, the presence of water droplets, and the tendency of particles to agglomerate or coalesce. The major methods employed for particle size determinations in emissions from pulp and paper mill sources are multistage cascade impaction and membrane filtration.

Bosch, Pilat, and Hrutfiord (26) describe the use of a multistage cascade impactor for particle size determination from kraft recovery furnaces over the range 0.5 to 20 μm (2×10^{-5} to 8×10^{-4} in) in diameter. The system is an internally located six-stage cascade impactor in which particles of progressively smaller diameter are collected on successive silicone-coated plates by passage through multihole plates with progressively smaller diameter holes. Sampling times vary from 30 seconds to 30 minutes, depending on the particulate loading of the source being measured.

The system must be calibrated for a given dust at a certain flow rate prior to collection to determine the approximate mean particle diameters for individual stages. Particle size determinations are made by gravimetric weighings of individual plates; the system of classification of particles is as percentage by weight within given sizes. Particles smaller than 0.5 μm (2×10^{-5} in) in diameter are collected on a filter following the impaction plates, as shown in Figure 17-12.

The National Council for Air and Stream Improvement has developed a method for collection of particles on a membrane filter for subsequent visual counting and sizing by means of an optical microscope (27). The system employs a parallel flow heated collection train with the membrane filter on one branch and a valving system on the other, as shown in Figure 17-13. The system must be hydrostatically balanced so that there is the same resistance to flow in both branches. It is then placed in the stack and heated to 93° C (200° F). This temperature is high enough to prevent condensation, but not so high as to damage the filter. The gas stream is first directed through the bypass system and then through the filter for 20 to 30 seconds to collect the particles. The technique is suitable only for sizing particles on a count basis, which is a time consuming procedure, and does not



1 CASCADE IMPACTOR ASSEMBLY
2 WATER BATH
3 IMPINGERS
4 THERMOMETER
5 DRY GAS METER
6 VACUUM GAUGE
7 VACUUM PUMP
8 GAS FLOW RATE REGULATOR

FIGURE 17-12

MULTISTAGE CASCADE IMPACTOR FOR PARTICLE SIZE DISTRIBUTION DETERMINATION (26)

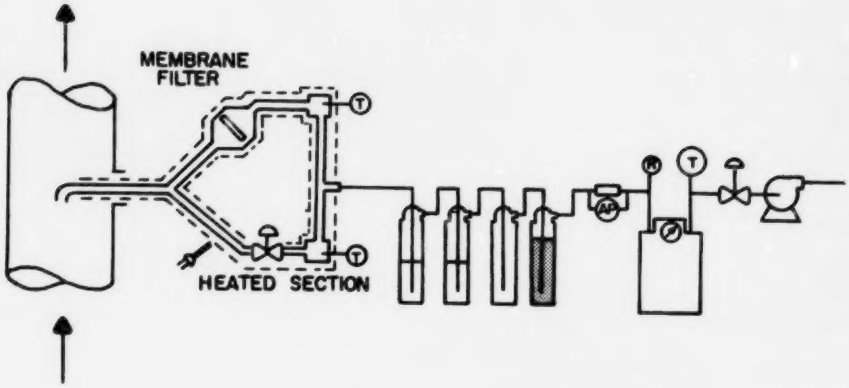

MEMBRANE FILTER
T
ΔP
T
T
HEATED SECTION

FIGURE 17-13

MEMBRANE FILTER SYSTEM FOR PARTICLE SIZE DISTRIBUTION DETERMINATION (27) allow determination of particle size distribution on a weight basis. But, the sample collection can be done in a short time interval, does not require the extensive precalibration required for the cascade impactor devices, and does not require prior knowledge of the dust density characteristics.

17.3.4 Continuous Monitoring

Continuous particulate monitoring is gaining increasing emphasis for determination of stack concentrations and emission rates. Methods now in use for particulate monitoring in the pulp and paper industry include wet chemical techniques, such as conductivity and specific ion determinations, and optical bolometry and transmissometry. Techniques which may become applicable in the future, include beta ray attenuation, piezoelectric crystallography, electronic sensing, optical nephelometry, holography, electric ion capture, and optical lasers, lidar, and radar (28).

17.3.4.1 Chemical Methods

Leonard (29) describes a wet chemical system for determining particulate emissions from a kraft recovery furnace on a continuous basis. The system operates on the principle that the increase in electrical conductivity of a liquid stream caused by the presence of sulfate ion is proportional to the total particulate loading, which is primarily Na_2SO_4. Flue gas is withdrawn from the duct at a predetermined average isokinetic velocity into a probe and contacted concurrently with deionized water, as shown in Figure 17-14. The soluble particulate matter is passed through a detection cell containing a conductivity probe and the

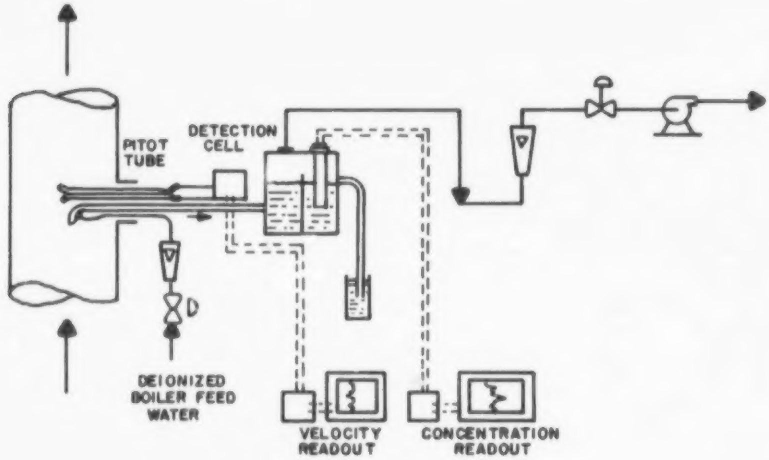


FIGURE 17-14

CONTINUOUS MONITORING OF PARTICULATE EMISSIONS WITH A CONDUCTIVITY CELL DETECTOR (29) gas is drawn off by a vacuum pump. The method is simple and inexpensive, but is nonspecific because any conductivity-producing substance can cause interference, e.g., SO_2 or CO_2 from the flue gas.

Tretter has developed a modification to the conductivity method for measuring particulate concentrations which alleviates conductivity interferences caused by the presence of SO_2 and CO_2 in the flue gas (30). The method uses a sodium ion-specific electrode to measure the sodium content of a water stream as an indicator of total particulate concentration. The system withdraws the gas sample through a probe and allows the absorption into water in a concurrent flow condenser by condensation of compressed steam, as shown in Figure 17-15. The liquid stream is then directed to a detection cell containing the sodium electrode where a liquid pH of 8.5 to 9.5 is maintained for maximum sensitivity. The system requires periodic maintenance, and, for calibration, a correlation between sodium ion level and total particulate concentration must be developed by using parallel batch tests.

17.3.4.2 Optical Determinations

Optical devices in use for particulate monitoring include internally located bolometers and transmissometers, where the degree of light attenuation is a function of the particulate concentration in the duct. The system directs a light beam across the duct to a detector where the resulting electrical signal is amplified, transmitted, and printed out on a recorder.

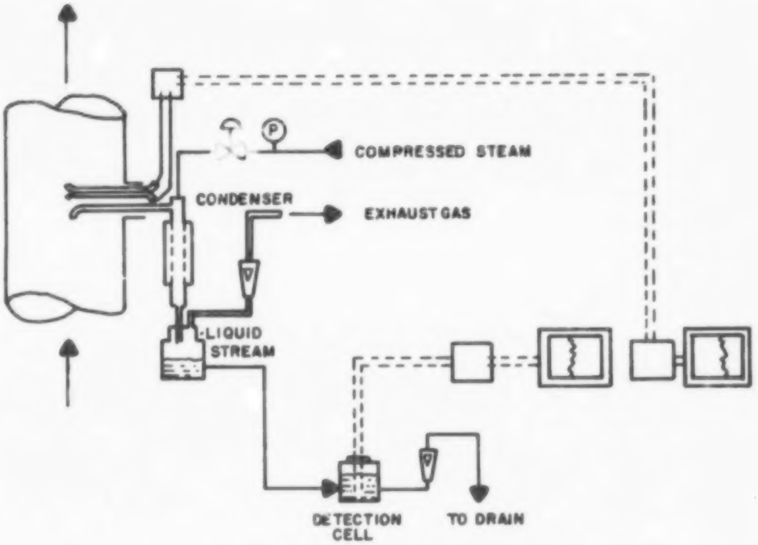


FIGURE 17-15

CONTINUOUS MONITORING OF PARTICULATE EMISSIONS WITH A SODIUM ION-SPECIFIC ELECTRODE (30)

The sensitivity and accuracy of optical stack monitoring devices is affected by path length, intensity, and wavelength of the light beam, moisture content as a function of temperature of the stack gas, particle size distribution, and particle mass concentration of the flue gas stream. (31).

Gansler describes the use of a bolometer for measuring particulate emissions from a kraft recovery furnace flue gas (32). The system uses a tungsten lamp with an optical band from approximately 500 to 2,500 nm. The device is suitable for measuring particle concentrations at levels below $29/m^3$ (0.9 gr/cu ft), and provides warnings of precipitator malfunctions. The device requires extensive prior calibration by parallel batch tests and also frequent lens cleaning.

Beutner describes the use of optical transmissometers for continuous particulate monitoring at a number of installations (33). The system employs a fixed length light beam with a wavelength of 300 to 800 nm, about the visible region of the spectrum. The gas stream passes between the beam and the detector. Fans are used to blow sufficient air across the surface to keep the lens surfaces clean. The device can be either permanently mounted or portable. The system is effective as an indication of particulate matter primarily of a size range of 0.1-1.0 μm (4 to 40×10^{-6} in). The system must be calibrated for the specific source by an extensive series of batch tests.

Optical particulate measurement devices are suitable for application to kraft recovery furnaces, coal- and wood-fired power boilers, and kraft lime kilns, and possibly ammonium and magnesium-base sulfite recovery furnaces.

They are particularly useful for providing warnings of possible particulate emission control equipment malfunctions and as indicators of combustion unit efficiencies for power boilers. They are also useful for emission monitoring for possible compliance with stack opacity standards, because optical transmittance is the property they measure. Their use is limited for mass emission monitoring because long-term correlations with batch tests must be determined under stable operating conditions. The lenses of the detectors tend to become obscure so that they can require frequent cleaning, and changes in particle size distribution can alter readings. The devices are probably most suitable for stacks with low particulate concentrations following high efficiency control devices where the particle size distribution is relatively uniform.

17.4 Odor Measurements

Measurements of odors is a major problem in the pulp and paper industry. The major chemical components that may cause a community odor nuisance are reduced sulfur compounds, such as H_2S, CH_3SH, CH_3SCH_3, and CH_3SSCH_3. These malodorous sulfur compounds and, possibly, other organic compounds are emitted from the digesters, evaporators, recovery furnace, smelt tank, lime kiln, and wastewater streams in kraft pulp mills. Under certain circumstances, SO_2 and organic sulfur compounds from sulfite pulp mills can also cause a community odor nuisance.

Odor measurement is an extremely complex task because of variations in the types and amounts of odorous gases present, variations in response between individuals, and variations within an individual with time because of his physical condition, smoking history, time of exposure, and prior history of exposures. Meteorological variables, such as temperature, humidity, wind velocity, and turbulence, can affect odor responses of individuals (34). Odorous gas molecules that are adsorbed on the surfaces of particles can travel for longer distances in a concentrated form and bring sharper responses than the odorous gas molecules alone (35).

17.4.1 Threshold Levels

The odor threshold levels for most malodorous sulfur compounds emitted from kraft pulp mill sources are between 1 and 10 ppb by volume, as shown in Table 17-4 (36):

TABLE 17-4
ODOR THRESHOLD LEVELS FOR
MALODOROUS SULFUR COMPOUNDS (36)

Sulfur Compound	Threshold ppm, by vol
H_2S	4
CH_3SH	2
CH_3SCH_3	4
CH_3SSCH_3	6
SO_2	3,000

The odorous gas levels for flue gas streams can be anywhere from 1,000 to 100,000 times as high as those observed at distances of up to 10 km (6 miles) from the kraft pulp mill.

The evaluation of odors can be made in terms of their character, intensity, pervasiveness, and acceptability. The intensity of an odor tends to increase with the logarithm of its concentration according to the Weber-Fechner law (37). Odor intensity levels can be rated on an arbitrary scale in values ranging from one to five, as shown in Table 17-5 (35).

TABLE 17-5
ODOR INTENSITY LEVEL EVALUATION SCALE

Arbitrary Number	Intensity Level
0	No Odor
1	Detectable
2	Faint
3	Noticeable
4	Strong
5	Overcoming

These levels can be used as reference scales for people on a panel in an attempt to provide some quantitative scale of odors.

17.4.2 Design Considerations

Major considerations in performing an odor threshold evaluation include the selection of human subjects, the sample collection methods, and the dilution techniques employed. The two general approaches to odor level measurement are:

1. Direct subjective organoleptic determination of odor threshold levels, and

2. Nonselective chemical determination of individual odorant concentrations by gas chromatography or other means.

Odor level measurements require careful collection and careful evaluation of samples.

An odor panel is normally selected as a group of people who have particular sensitivity, accuracy, speed, and reproducibility for evaluating the odor threshold and intensity levels for the gases being measured. The odor panel goes through a training program for a specific period, and then is used to test stack gas mixtures. Panelists may undergo testing for 15 minutes at a time with rest periods of at least 30 minutes to avoid olfactory fatigue. It is normally best to expose panelists to low concentrations before high concentrations to avoid deadening their response. Prince and Ince find that responses can vary as much as 40 percent for individual panelists on any given day and 20 percent for a panel of observers (38).

Gas sample collection may be by direct piping of the flue gas to a panel to minimize potential losses, but this may not always be feasible. Samples of stack gas or ambient air may also be collected in plastic bags, heated evacuated bottles, or in syringes. Odorous gas losses by solution in condensed water vapor, or physical absorption or chemical reaction with container walls, are to be eliminated normally by the use of inert wall materials such as Teflon.

17.4.3 Dilution Techniques

Two publications by the National Council for Air and Stream Improvement present extensive discussions of systems for dilution of odorous gases to facilitate evaluation of odorant intensity levels (39) (40). The major techniques for evaluation of odor threshold levels are:

1. Static progressive dilution using glass syringes.
2. Dynamic dilution of odorous gases using odor-free air,
3. Dilution of odorous air with odor-free air by respiration, and
4. Vaporization of odorous compounds in a continuous flow system.

The American Society for Testing and Materials specifies progressive static dilutions in glass syringes. The same is first collected in a 100 cm^3 glass syringe (41). The flue gas sample then is diluted in the laboratory by adding aliquots of known volume to other syringes of this same size. The aliquots then are given to an odor panel in order of decreasing dilution (increasing odorant concentration) to evaluate odor threshold levels and odorant intensities. The syringes must be cleared after use and dried to avoid contamination of future samples.

Several systems are available for dynamic dilution of odorous gases by means of odor-free air for subsequent observation by a panel. Normally, the odorous gas sample must be collected in some type of container before being added to the dilution system in a laboratory. Field exposure of subjects prior to odor level evaluations can lead to olfactory fatigue and resultant insensitivity to odorous gas concentrations. Cederlof (42) describes a system in which odorous gas samples are collected from kraft mill flue gases in flexible plastic bags and returned to the laboratory where they are diluted with purified air for exposure to a panel inside a hood, as shown in Figure 17-16. The inlet odorant gas flow is controlled at a constant rate by a limiting flow capillary, while the air flow rate is measured by a rotometer.

Direct observations of odor levels in the atmosphere or from flue gas streams by means of a progressive dilution device known as a "Scentometer" have been made. The device is powered by the observer's respiration. The system draws in variable amounts of odorous gas or air through an adjustable orifice followed by dilution with air which has been purified by

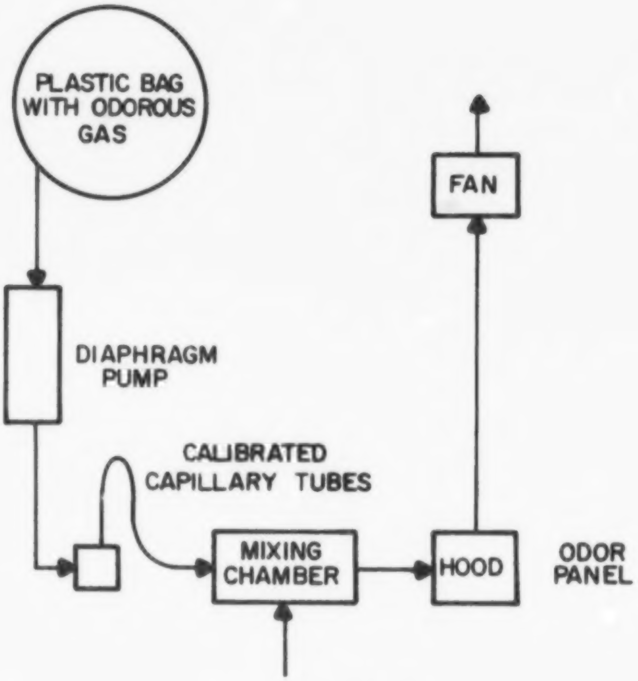


FIGURE 17-16
SWEDISH DYNAMIC DILUTION SYSTEM FOR ODOR LEVEL EVALUATION (42)

activated carbon, as shown in Figure 17-17 (43). The relative amounts of odorous gas and purified air are governed by a series of four orifices which provide for dilution factors of 2, 7, 31, and 170 times, respectively. The procedure starts from the greatest degree of dilution and works progressively toward lesser dilution until the odor threshold is observed.

17.5 Mobile Laboratories

Mobile laboratories provide the capability of making comprehensive evaluations of ambient and source concentrations for gaseous and particulate materials in the field. Mobile laboratories used for air pollution studies should be equipped with instrumentation for continuous measurement of sulfur compounds, a gas chromatograph for analyses of specific compounds, analytical equipment for additional constituents, such as oxides of nitrogen, and particulate sampling equipment.

Walther and Amberg describe a mobile laboratory mounted in a van that has the capability of monitoring malodorous sulfur compounds. It uses two gas chromatographs in parallel equipped with thermal conductivity and flame ionization detectors, respectively (44). The sample handling system consists of a heated ceramic probe and a Teflon electrically traced

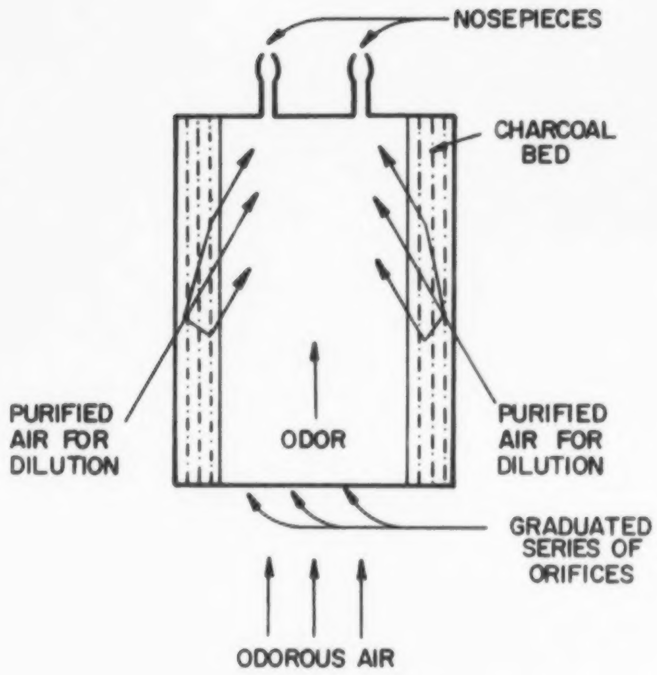

NOSEPIECES
CHARCOAL BED
PURIFIED AIR FOR DILUTION
ODOR
PURIFIED AIR FOR DILUTION
GRADUATED SERIES OF ORIFICES
ODOROUS AIR

FIGURE 17-17

SCENTOMETER DILUTION SYSTEM FOR ODOR THRESHOLD EVALUATION (43)

sampling line for carrying the flue gas from the stack to the instruments. The van proved too small and had to be placed in a permanent location, thus negating its mobility.

Mulik, Stevens, and Baumgardner report on a mobile laboratory mounted in a trailer which employed flame photometric detectors for measuring reduced sulfur compounds (45). Samples were taken at a rate of 50 l/min (1.8 cfm) from a source gas through a 0.63 cm diameter and 76 m long (0.25 inch by 250 ft) electrically traced Teflon sampling line maintained at 182° C (360° F) to prevent moisture condensation. The gas chromatograph employed a 10-port sample valve with a 10 cm^3 (0.6 cu in) sample loop actuated on a 10-minute sequence for sample injection. A dynamic dilution system was used for sample dilution factors covering a range from 10 to 1,000,000 to 1, depending on the requirements for optimum sensitivity with the flame photometric detector.

17.5.1 NCASI System

The National Council for Air and Stream Improvement employs a trailer for mobile emission sampling of kraft pulp mills (46). The sample system consists of a heated ceramic sample probe, a heated, electrically traced Teflon sampling line, and a heated conditioning box for dilution of the sample, as shown in Figure 17-18. The gas is withdrawn at a greater rate than that required for the instruments in order to minimize retention time in the sample lines. The instrumentation consists of two coulometric titrators with a furnace for sulfur gas analysis and a gas chromatograph equipped with flame ionization and flame photometric detectors. Total cost of the entire system when constructed was approximately $30,000, and it required two men for its operation.

The sampling handling system employs withdrawal of the sample gas at a rate of approximately 1 l/min (0.035 cfm) through a probe heated to 150° C (300° F) to evaporate water droplets to alleviate droplet entrainment in the sampling lines. The electrically traced 0.63 cm (0.25 inch) diameter Teflon sampling line 33 or 66 m (100 or 200 ft) length is heated to 110 to 121° C (230 to 250° F) to prevent moisture condensation. The gas stream then passes into a heated sample conditioning box, where portions of the gas stream are bled off to either the continuous sulfur monitors or the gas chromatograph, while the remainder passes to a large glass carboy acting as a condensate trap to avoid damage to the pump. The sample gas stream leading to continuous sulfur analyzers can be diluted by factors from zero to 25.

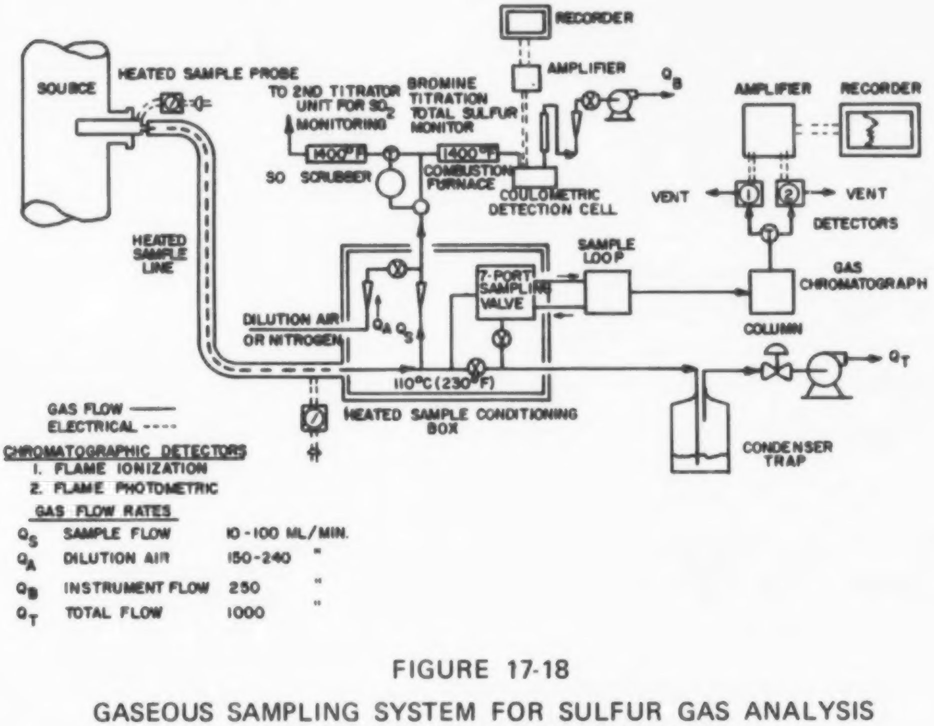

RECORDER
AMPLIFIER
Q_B
SOURCE
HEATED SAMPLE PROBE
TO 2ND TITRATOR UNIT FOR SO_2 MONITORING
BROMINE TITRATION TOTAL SULFUR MONITOR
AMPLIFIER
RECORDER
1400°F
1400°F
SO SCRUBBER
COMBUSTION FURNACE
COULOMETRIC DETECTION CELL
VENT
1
2
VENT
DETECTORS
HEATED SAMPLE LINE
SAMPLE LOOP
7-PORT SAMPLING VALVE
GAS CHROMATOGRAPH
DILUTION AIR OR NITROGEN
Q_A
Q_S
COLUMN
Q_T
110°C (230°F)
HEATED SAMPLE CONDITIONING BOX
CONDENSER TRAP
GAS FLOW ——
ELECTRICAL ----
CHROMATOGRAPHIC DETECTORS
1. FLAME IONIZATION
2. FLAME PHOTOMETRIC
GAS FLOW RATES
Q_S SAMPLE FLOW 10-100 ML/MIN.
Q_A DILUTION AIR 150-240 "
Q_B INSTRUMENT FLOW 250 "
Q_T TOTAL FLOW 1000 "

FIGURE 17-18

GASEOUS SAMPLING SYSTEM FOR SULFUR GAS ANALYSIS
IN NCASI MOBILE LABORATORY (46)

The continuous sulfur analysis system either splits the gas flow into two parallel streams for simultaneous measurement of both total sulfur and TRS, or passes a single stream through an SO_2 selective scrubber containing either $KHC_8H_4O_4$ or citric acid ($C_6H_8O_7$). The gas then passes through parallel quartz combustion furnaces heated to 760° C (1,400° F) for oxidation of the reduced sulfur compounds to SO_2, which then is measured by means of parallel bromine coulometric titrators. The difference between the signals for total sulfur (SO_2 + H_2S + organic sulfur) and TRS (H_2S + organic sulfur) is taken as being proportional to the SO_2 concentration of the flue gas stream. The separation and identification of specific sulfur compounds is made by periodic injection of samples of given volume through the sample loop. The sample size is governed by the volume of the sample loop. The sample gas then passes through a separation volume for analysis by either flame ionization or flame photometric detection.

17.5.2 Rayonier System

Waddington describes the mobile laboratory constructed by ITT-Rayonier, Inc., for monitoring paper mill emissions and ambient air from a 10.7 m (35 foot) truck trailer (47). The system has both particulate and gaseous sampling trains and sample handling systems, as shown in Figure 17-19. The particulate systems consist of an EPA train for total particulate analyses and an Andersen sampler for particle size determination. The gaseous sampling system consists of parallel heated sampling lines and a sample conditioning system to provide for dilutions with air by factors of 10 to 10,000. The gaseous instrumentation consists of continuous monitors for reduced sulfur compounds, SO_2, CO, oxides of nitrogen, and hydrocarbons. The gas chromatograph is equipped with flame ionization and flame photometric detectors.

The sample handling system for source gas analyses employs withdrawal of the sample gas through heated filters located outside the stack through an electrically traced heated Teflon sampling line of 0.95 cm (3/8 in) diameter 33 or 66 m (100 or 200 ft) in length. The gas stream passes through at a rate of 100 to 160 l/min (3.5 to 5.7 cfm) and small portions then pass out into a series of as many as three consecutive dilution stages in a heated sample conditioning box for dilutions from 15 to 1,500 to one. Portions of the gas streams, including SO_2, NO_X, CO, and TRS, are routed through three separate channels to several detectors for measuring individual gaseous products.

Ambient monitors are used for SO_2 and NO_2. The gas chromatograph employs parallel flame photometric and flame ionization detectors with a 10-port sampling valve for sample injection.

For particulate sampling, two parallel EPA-type sampling trains can be used on the inlets and outlets of particulate emission control devices. Either can be fitted with Andersen cascade impactors that can be internally or externally located for particle size determinations. Ambient particulate measurements can be made with several high volume

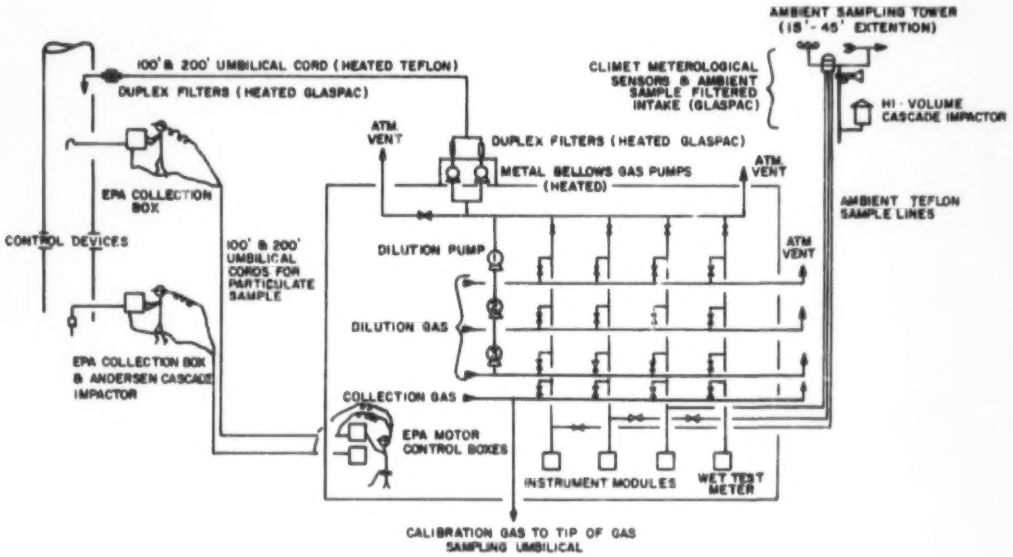

AMBIENT SAMPLING TOWER (15'-45' EXTENTION)
100' & 200' UMBILICAL CORD (HEATED TEFLON)
DUPLEX FILTERS (HEATED GLASPAC)
CLIMET METEROLOGICAL SENSORS & AMBIENT SAMPLE FILTERED INTAKE (GLASPAC)
HI-VOLUME CASCADE IMPACTOR
ATM. VENT
DUPLEX FILTERS (HEATED GLASPAC)
METAL BELLOWS GAS PUMPS (HEATED)
ATM. VENT
EPA COLLECTION BOX
AMBIENT TEFLON SAMPLE LINES
CONTROL DEVICES
100' & 200' UMBILICAL CORDS FOR PARTICULATE SAMPLE
DILUTION PUMP
ATM VENT
DILUTION GAS
EPA COLLECTION BOX & ANDERSEN CASCADE IMPACTOR
COLLECTION GAS
EPA MOTOR CONTROL BOXES
INSTRUMENT MODULES
WET TEST METER
CALIBRATION GAS TO TIP OF GAS SAMPLING UMBILICAL

FIGURE 17-19

PARTICULATE AND GASEOUS SAMPLE HANDLING SYSTEMS
FOR ITT-RAYONIER MOBILE LABORATORY (47)

suspended particulate samplers carried in the van. A weather station is also carried in the van for meteorological studies of wind speed, wind direction, and air temperatures. Total cost of the entire van was about $250,000, and its operation requires three men.

17.6 Economics

An important factor in the design and operation of continuous stack monitoring systems is the cost of the necessary equipment. Auxiliary equipment, such as recorders, sampling lines, fittings, and other appurtenances, must be included in the total cost. Failure to properly account for the auxiliaries can cause variations in prices between different systems. Approximate ranges in capital cost for gaseous monitoring equipment are listed in Table 17-6, and for particulate monitoring equipment in Table 17-7. The figures listed are expressed as approximate ranges only; exact figures must be determined by direct quotations from specific manufacturers.

TABLE 17-6
APPROXIMATE CAPITAL COSTS FOR CONTINUOUS GASEOUS STACK MONITORING INSTRUMENTATION

Instrument Type	Pollutants Measured	Capital Cost dollars
Electrolytic Conductivity	SO_x	1,000-2,000
Ultraviolet Spectrophotometry	SO_x, NO_x, TRS	2,500-10,000
Electrochemical Transducer	SO_x, NO_x, CO, TRS	3,000-9,000
Coulometric Titration	SO_x, TRS	5,000-8,000
Flame Ionization	Organic	2,000-7,000
Chemiluminescence	NO_x	5,000-7,000
Flame Photometry	SO_x, TRS	4,000-8,000

TABLE 17-7
APPROXIMATE CAPITAL COSTS FOR CONTINUOUS PARTICULATE STACK MONITORING INSTRUMENTATION

Instrument Type	Detection Principle	Capital Cost dollars
Optical Bolometer	Optical	2,000-3,000
Optical Transmissometer	Optical	5,000-7,000
Electronic Sensing	Electrical	6,000-7,000
Beta-Ray Attenuation	Radiation	10,000-20,000

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APPENDIX A

GLOSSARY OF SYMBOLS

Symbol	Definition
B&W	Babcock & Wilcox
BOD	biochemical oxygen demand
BOD_7	biochemical oxygen demand as determined by 7-day test
BLO	black liquor oxidation
BLRBAC	Black Liquor Recovery Boiler Advisory Committee
BP	boiling point
BHV	bomb heat values
BD	bone dry
BCRC	British Columbia Research Council
BTU	British thermal unit
cm	centimeter
CE	Combustion Engineering
ACE	CE system of contact evaporation using combustion air
LAH	CE system of evaporation using Laminaire air heaters
cfm	cubic feet per minute
cfs	cubic feet per second
cu ft, ft^3	cubic foot
m^3	cubic meter
m^3/h	cubic meters per hour
°C	degree Celsius
°F	degree Fahrenheit
°K	degree Kelvin
DO	dissolved oxygen
DS	dry solids
ft	foot
fpm	feet per minute
fps	feet per second
fl oz	fluid ounce
gal	gallon
gpm	gallons per minute
gr	grain
g	gram
h, hr	hour
hp	horsepower
in	inch

Symbol	Definition
ID	induced draft
SI	International System of Units ("metric system")
kcal	kilocalorie
kg	kilogram
kJ	kilojoule
km	kilometer
kW	kilowatt
LK	lime kiln
MJ	megajoules
MPa	megapascal (= 10^6 kg · m/sec^2 per m^2)
t	metric ton
µm	micrometer
mm	millimeter
mg	milligram
mV	millivolt
min	minute
ng	nanogram
nm	nanometer
NCASI	National Council for Air and Stream Improvement
NSSC	neutral sulfite semi-chemical (process)
NCG	noncondensable gases
R	organic chemical radical
NO_x	oxides of nitrogen
SO_x	oxides of sulfur
ppb	parts per billion
ppm	parts per million
lb	pound
pcf	pounds per cubic foot
psia	pounds per square inch, absolute pressure
psig	pounds per square inch, gauge pressure
psi	pounds per square inch
RF	recovery furnace
s, sec	second
ton	short ton (2000 lb)
SSL	spent sulfite liquor
std	standard
scf	standard cubic foot
scm	standard cubic meter
sdcf	standard dry cubic foot
SBLO	strong black liquor oxidation

Symbol	Definition
TRS	total reduced sulfur
w.g.	water gauge
W	watt
WBLO	weak black liquor oxidation
yd	yard
yr	year

APPENDIX B

CHEMICAL FORMULAS

Acetic Acid	CH_3COOH
Acetone	CH_3COCH_3
Acrolein	CH_2CHCHO
Ammonia	NH_3
Ammonium bisulfite	NH_4HSO_3
Ammonium sulfate	$(NH_4)_2\ SO_4$
Ammonium sulfite	$(NH_4)_2\ SO_3$
Arsenic	As
Beryllium	Be
Boric acid	H_3BO_3
Bromine, molecular bromine	Br, Br_2
Cadmium	Cd
Cadmium sulfate	$CdSO_4$
Calcium bisulfite	$Ca(HSO_3)_2$
Calcium Oxide (lime)	CaO
Calcium sulfite	$CASO_3$
Carbon dioxide	CO_2
Carbon monoxide	CO
Carbonic Acid	H_2CO_3
Carbonyl hydrogen sulfide	$COSH$
Carbonyl sulfide	COS
Chlorine dioxide	ClO_2
Chlorine, molecular chlorine	Cl, Cl_2
Citric Acid	$C_6H_8O_7$
Dimethyl disulfide	CH_3SSCH_3
Dimethyl Sulfide	CH_3SCH_3
Ethanol, Ethyl alcohol	CH_3CH_2OH
Ferric chloride	Fe_2Cl_6
Ferrous sulfide	FeS
Fluorine	Fl
Formaldehyde	$HCHO$
Hydrobromic acid	HBr
Hydrochloric acid	HCl
Hydrogen, molecular hydrogen	H, H_2
Hydrogen peroxide	H_2O_2
Hydrogen sulfide	H_2S
Lead	Pb

Magnesium bisulfite	$Mg(HSO_3)_2$
Magnesium hydroxide	$Mg(OH)_2$
Magnesium oxide, magnesia	MgO
Mercury	Hg
Methane	CH_4
Methanol, methyl alcohol	CH_3OH
Methyl mercaptan, methanethiol	CH_3SH
Nitric oxide	NO
Nitrogen dioxide	NO_2
Nitrogen, molecular nitrogen	N, N_2
Nitrogen oxides	NO_x
Oxygen, molecular oxygen, ozone	O, O_2, O_3
Phosphorus	P
Potassium acid phthalate	$KHC_8H_4O_4$
Selenium	Se
Silver nitrate	$AgNO_3$
Sodium bicarbonate	$NaHCO_3$
Sodium hydrogen sulfide	$NaHS$
Sodium bisulfite	$NaHSO_3$
Sodium carbonate	Na_2CO_3
Sodium chloride	$NaCl$
Sodium chlorite	$NaClO_2$
Sodium hydroxide	$NaOH$
Sodium mercaptide	CH_3CH_2SNa
Sodium sulfate	Na_2SO_4
Sodium sulfite	Na_2SO_3
Sodium thiosulfate	$Na_2S_2O_3$
Sulfur	S
Sulfur dioxide	SO_2
Sulfur trioxide	SO_3
Sulfuric acid	H_2SO_4
Vanadium	V
Vanadium pentoxide	V_2O_5
Water	H_2O
Zinc	Zn

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